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SYNTHETIC AND N.M.R. STUDIES OF POLYORGANOPHOSPHORUS COMPOUNDS

A Thesis submitted to the Council for National Academic Awards in Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy.

by

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ABSTRACT

Synthetic and N.M.R. Studies of Polyorganophosphorus Compounds.

P.G.Patel.

A new five-membered cyclic tertiary diphosphine has been synthesised, $PhPCH(=CH_2)PPhCH_2CH_2$ (X). Cis and trans isomers were observed; and the trans isomer (Xb) has been isolated and fully characterised by P-31, H-1 and C-13 n.m.r. spectroscopy.

By the base-catalysed addition reaction of primary and secondary phosphines to the C=C double bond of (Xb), novel tritertiary cyclic polyphosphines $PhPCH(CH_2PHPh)PPhCH_2CH_2$ (VII), $PhPCH(CH_2PHC_6H_2((C(CH_3)_3)PPhCH_2CH_2$ (VIII), $PhPCH(CH_2PPh_2)PPhCH_2CH_2$ (IX) and $PhPCH(CH_2PPh(n\text{-}Bu))PPhCH_2CH_2$ (XI), pentatertiary $[PhPCH_2CH_2PPhCHCH_2]_2PPh$ (XII) and $PhPCH_2CH_2PPhCH\text{-}CH_2PPh\text{-}CH_2CH(PPh_2)_2$ (XIII) and hexatertiary $[PhPCH_2CH_2PPhCHCH_2PPhCH_2]_2CH_2$ (XVI) have been synthesised, and the analysis of their spectra confirms the trans nature of the cyclic diphosphine (Xb). The Group Contribution Concept of Grim et al was extended to account for phosphorus shielding in these cyclic compounds.

Due to the trans configuration of the phosphorus lone pairs of (Xb), all but one of the cyclic polyphosphines reveal the presence of two or more diastereoisomers. This leads to complicated P-31 n.m.r. spectra which have nonetheless been analysed. In the case of (XVI), the complex nature of the P-31 n.m.r. spectrum required a 2D J-resolved experiment to reveal the presence of six diastereoisomers.

The coordination chemistry of these compounds with a range of metal substrates was assessed by using sulphurisation reactions as a model and a range of products were obtained and identified. It thus appears that these polyphosphorus compounds have considerable potential as ligands.

The structures and bonding of lithiated tricoordinated organophosphorus compounds in solution have been investigated by P-31 and Li-7 n.m.r. spectroscopy and it has been possible to confirm the proposed dimeric structure of $[Ph_2PLi]_2$. By analysis of the C-13 n.m.r. spectrum of $[Ph_2PLi]_2$ at low temperature the $^2J(P\text{-}P)$ was found to be large. This was confirmed by the formation of an unsymmetrical dimeric lithiated phosphine $[Ph_2PLi_2P(n\text{-}Bu)_2]$, which permitted the direct measurement of $^2J(P\text{-}P)$.

Additionally, a variety of primary and secondary phosphines have been lithiated. Their structures, in many cases, have been deduced by low temperature analysis of P-31, Li-7 and Li-6 n.m.r. spectra, e.g. $["i\text{-}Pr_2PLi"]_4$, $["n\text{-}Bu_2PLi"]_2$, $["PhMePLi"]_2$, $["PhEtPLi"]_2$, $["Ph(n\text{-}Bu)PLi"]_2$, $["(2\text{-}MeC_6H_4)_2PLi"]_2$, $["(Ph(Li)P(CH_2)_3P(Li)Ph"]_2$ and $["(Ph(Li)P(CH_2)_{2,4 \text{ and } 6}P(Li)Ph"]_n$.

Acknowlegements.

I would like to thank my supervisor Professor William McFarlane who suggested the initial line of work, for his considerable help and encouragement throughout this study and who has been a constant source of guidance and inspiration.

I would also like to thank other colleagues of mine who have been of assistance, in particular Dr.B.Wood for his help in recording some of the n.m.r. spectra.

In addition I would like to thank the S.E.R.C. for the Studentship grant.

Statement of Advanced Studies.

The author has attended and contributed to national and international meetings of the Royal Society of Chemistry, in particular those associated with n.m.r. spectroscopy. Throughout the study constant reference was made to relevant publications such as Specialist Periodical Reports in Nuclear Magnetic Resonance, the Dalton Transactions of the Journal of the Chemical Society, the Journal of the American Chemical Society and other journals were consulted regularly in order to keep abreast of the latest advances in chemistry in general.

CONTENTS

CHAPTER 1

INTRODUCTION

INTRODUCTION

The interest in cyclic organophosphorus chemistry has grown considerably in the past three decades. In 1950 when Kosolapoff[1] published his comprehensive monograph on organophosphorus chemistry only about twenty heterocyclic structures were mentioned. By 1970 when F.G. Mann[2] published a review on heterocyclic systems 150 compounds were known. Since the 1970's, the interest in these class of compounds has developed rapidly, with lengthy reviews[3-9] published in specialised fields. The work has concentrated on the development of new synthetic routes to the cyclic organophosphorus compounds which can be fully characterised as a result of advances in modern spectroscopic techniques such as n.m.r., i.r. X-Ray diffraction, u.v. and mass spectrometry.

This thesis consists of two sections: the second details the work conducted on lithiated organophosphines and discusses the synthetic route taken in the preparation of these compounds and the use of multinuclear n.m.r. to determine their structures; the first part discusses the synthesis and characterisation by n.m.r. spectroscopy of a new five-membered cyclic organophosphine and a series of related cyclic polyorganophosphines.

The following section reviews the known cyclic organophosphorus compounds and examines the use of n.m.r. spectroscopy to characterise the new five-membered cyclic organophosphine and cyclic polyorganophosphines.

PHOSPHORUS CHEMICAL SHIFTS.

Considerable work has been conducted to determine the factors which influence the phosphorus chemical shifts of organophosphorus compounds.[10-16] It is generally accepted that the three factors which affect the position of the phosphorus chemical shift of (acyclic) organophosphorus compounds are:-

(a). the degree of occupation of the d-orbitals by π-electrons;

(b). the electronegativity of the substituents;

(c). the variation of the bond angles about the phosphorus nucleus, which is dependent upon the nature of organic substituents on the phosphorus nucleus.

This thesis is principally concerned with tricoordinated organophosphines and hence contributions to the chemical shift values by (a) and (b) are relatively insignificant, with (c) being the dominant factor.

Tricoordinate phosphorus compounds have hybridised orbitals: the σ-bonds are predominantly $\underline{p}^3$ in character, but have some $\underline{s}$ nature; hence the 'lone pair' $\underline{3s}$ electrons are involved in bonding. However, they are not of pure $\underline{sp}^3$ character. Since the organophosphines described here involve the occupation of the $\underline{p}$-orbitals and not the $\underline{d}$-orbitals, contributions from factor (a) do not have to be considered.

Variations in the contributions made by factor (b) to the phosphorus chemical shifts of organophosphines with alkyl and aryl substituents should be negligible. It has

been found that the electronegativities of a series of alkyl groups lie very close together (between 2.34 and 2.39)[17,18], and are close to the electronegativity of phosphorus with hybridised p -orbitals, which has a electronegativity of 2.38. Hence, chemical shift variations, resulting from the electronegativity effect of these groups and resultant electron density changes at the phosphorus nucleus, are insignificant.

The nature of the phosphorus-bonds is dependent upon both bond polarity and molecular geometry, and any variation in bond angles at the phosphorus nucleus results in an alteration of its surrounding electron density. Changes in geometry become more important when the three bond polarities (including unshared 3s electrons) differ significantly from each other and this is reflected in a range of chemical shift values.[14]

Additionally, work conducted by Grim et al[19], has shown how variations in observed phosphorus chemical shifts, which cannot be solely explained by factor (c), are better understood by the change in electron density resulting from the shielding effect of an alkyl group contribution (G.C.) to the electron density. This may be explained in terms of hyperconjugation within the molecule via the α-protons i.e. $[R_2\dot{\ddot{P}} - CR_2\overset{\alpha}{H} \longrightarrow R_2\dot{\ddot{P}} = CR_2\overset{\alpha}{H}]$, which results in an increased electron density at the phosphorus nucleus. Thus, the greatest increase in the shielding effect about the phosphorus nucleus would be in those tertiary phosphines possessing the largest number of α-protons. This result is confirmed when a methyl group is substituted for an

α-proton on the α-carbon of the alkyl group. Here, the group contribution is decreased due to the loss of the hyperconjugative proton and hence a deshielding effect is observed with a shift to the high frequency region (methyl groups alone would be expected to show shielding inductive effects).

β-proton substitution results in the expected shielding of the phosphorus nucleus due to the inductive effect of the methyl group, leading to a low frequency shift. Substitution of protons further down the alkyl chain has less effect upon the group contribution.

The significant result of this study was the recognition of a definite numerical contribution to the phosphorus chemical shift value by the substituent groups present. Using Equation 1.1. below, the group contribution by alkyl or aryl groups can be calculated and used to predict phosphorus chemical shift values of organophosphines to a good approximation.

$$G.C. = -21 + 14\,\beta C - 3\,\gamma C. \qquad \text{EQUATION 1.1}$$

(βC and γC are the number of β and γ carbon atoms).

In this thesis it will be shown that this concept can be extended to cyclic organophosphorus systems.

PHOSPHORUS CHEMICAL SHIFTS OF CYCLIC POLYORGANOPHOSPHORUS COMPOUNDS.

(A). CYCLIC POLYPHOSPHINES.

Table 1.1. shows the correlation between ring size and observed chemical shift for cyclic polyphosphines $(RP)_n$[20], where n = 3, 4, 5 or 6 and R = alkyl or aryl group. The phosphorus chemical shifts are found to lie in the following regions:-

(1). P_3 $\delta(P)$ = +145.1ppm [only one species examined, R = Et];

(2). P_4 $\delta(P)$ = +72.9ppm to +57.3ppm;

(3). P_5 $\delta(P)$ = -17.0ppm to +4.0ppm;

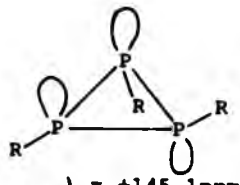
(4). P_6 $\delta(P)$ = +22.0ppm R = Ph.

(See Fig. 1.1).

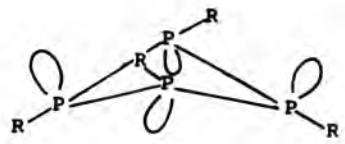
Systems where n = 7, 8 and 9 have been prepared, and have either norbornyl type frameworks, or consist of two rings joined by phosphorus-phosphorus bonds. In these systems, the phosphorus chemical shifts are found to fall within the range of the known acyclic compounds. Solvent effects upon $\delta(P)$ are not large in this class of compounds.

Table 1.1. : ^{31}P n.m.r. chemical shifts of cyclic polyphosphines, $(RP)_n$[20].

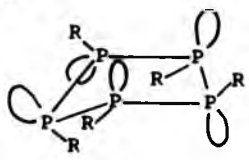
R	RING SIZE	SOLVENT	$\delta(^{31}P)$, ppm
Ph	6	THF	+22.0
Me	5	NEAT	-18.8
Et	5	NEAT	-16.0
Ph	5	NEAT	+4.7
t-Bu	4	C_6D_6	+57.3
i-Pr	4	C_6D_6	+61.8
Et	4	NEAT	+72.9
Et	3	$(EtP)_4$	+145.1



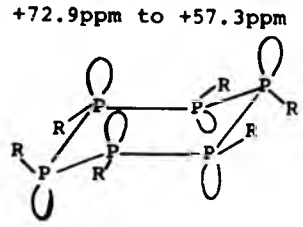
$\delta(P_{n=3})$ = +145.1ppm



$\delta(P_{n=4})$ = +72.9ppm to +57.3ppm



$\delta(P_{n=5})$ = -17.0ppm to +4.0ppm



$\delta(P_{n=6})$ = +22.0ppm

Fig. 1.1. : Diagrammatic representation of cyclic polyphosphines.

(B). CYCLIC POLYORGANOPHOSPHORUS COMPOUNDS.

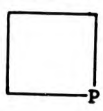
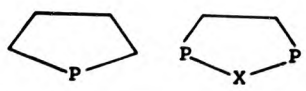
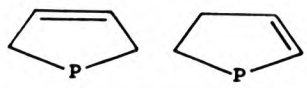
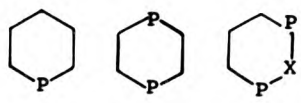
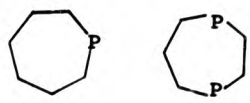
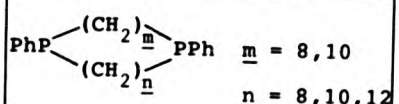
Cyclic organophosphorus species containing phosphorus and saturated carbon atoms are known and are based upon carbon ring systems. Most reports are concerned with the derivatives i.e. halide salts, sulphurised or oxygenated species, with only a few of the parent compounds having been isolated.[21-23]

The majority of the ring compounds for which considerable data are available contain, in addition to the phosphorus and carbon atoms, some other heteroatoms e.g. nitrogen, oxygen or sulphur. However, rings containing only phosphorus and carbon atoms are known and range from the three- to seven-membered cycles as well as the sixteen-, eighteen- and twenty-membered rings. Table 1.3. presents a selection of such compounds with differing ring sizes. Phosphorus n.m.r. spectral data on the majority of these compounds is either minimal or unreported. From the information that is available for these ring systems, there is found to be no obvious correlation between ring size and phosphorus chemical shift values, in contrast to the position regarding the cyclic polyphosphines $(RP)_n$.

(a). THREE- AND FOUR-MEMBERED RING SYSTEMS.

The three membered rings,[5,8,9,23-29] like their carbon counterparts, are very reactive and work other than that reported in Table 1.3. is very scarce. Likewise, synthetic limitations and the erstwhile unavailability of high

Table 1.2. : Nomenclature for cyclic organophosphorus compounds.

NAME	RING SIZE	STRUCTURE
PHOSPHIRANE	3	
PHOSPHETANE	4	
PHOSPHOLANE	5	
PHOSPHOLENE	5	
PHOSPHORINANE	6	
PHOSPHETANE	7	
MACROCYCLIC	>8	 m = 8,10 n = 8,10,12

resolution n.m.r. spectrometers account for the scarcity of phosphorus n.m.r. spectral data concerning the four membered rings.[30-33]

(b). FIVE-MEMBERED RING SYSTEMS-PHOSPHOLANES.[4,5]

(1). CONTAINING ONE PHOSPHORUS ATOM.

Five-membered rings containing only one phosphorus atom are stable and can be prepared readily. It has been found that for the cyclic phospholanes the phosphorus chemical shifts correspond well with those of the analogous acyclic phosphines. Work conducted by Breen et al[34] on the determination of phosphorus chemical shifts of five-membered cyclic tertiary phospholanes and phospholenes has shown that the Group Contribution concept can be applied to these systems.

It has been found that for these cyclic systems the phosphorus chemical shifts which can be predicted are comparable with those in analogous acyclic systems.

The results from measurements of phosphorus chemical shifts of a series of 1- and 1,3 - substituted phospholanes (Fig. 1.3), indicated a definite ring contribution. The ring contribution made by the 1-methylphospholanes was +11ppm, compared with the analogous acyclic system which consists of two ethyl moieties having a group contribution of +14ppm (G.C. of C_2H_5 = +7ppm).

FIG 1·2.

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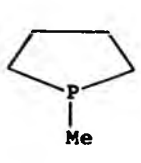
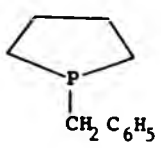


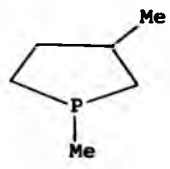
(a)

δ(P) = -32.0ppm



(b)

δ(P) = -14.4ppm



(c)

$\delta(P_{\underline{cis}})$ = -33.4ppm

$\delta(P_{\underline{trans}})$ = -33.8ppm

Fig. 1.3. : ^{31}P chemical shifts of a series of 1-methylphospholanes.

Where cis and trans isomers were present in these systems, the two phosphorus chemical shift values differed from each other, a fact which could not be predicted by group contribution effects alone. The proposed explanation for these results is that steric effects may lead to bond angle distortions, and there may be conformational differences. Results from the 3-phospholene systems having β-substituted methyl groups (Fig. 1.4), showed a greater than predicted deshielding effect. This was enhanced even further for the 2-phospholene system and is attributed to an anisotropic interaction between the double bond and the phosphorus lone pair of electrons.

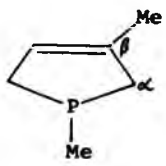


Fig. 1.4. : Representation of β-substituted 3-phospholene.

(2). CONTAINING TWO PHOSPHORUS ATOMS.

There are few phospholanes containing two phosphorus atoms, and those that have been reported are shown in Table 1.3. Of these, only 1,3-diphospholane has been investigated in any detail by phosphorus n.m.r. spectroscopy.[35] Thus, comparison of phosphorus n.m.r. spectral data known for the diphospholanes with that obtained for the species prepared and analysed in this thesis, using the five-membered ring system, is limited.

The diphospholanes indicate the presence of *cis* and *trans* isomers and their phosphorus chemical shift values are found to depend upon the configuration of the isomers. In nearly all cases, the *cis* isomers have chemical shift values to high frequency of the *trans* isomers. The magnitudes of the shifts tend to be quite small, but they are significantly different. In many of these systems where stereoisomers are predicted, they have not been distinguished, thus reducing the amount of phosphorus n.m.r. spectral data which can be used for comparisons.

(c). SIX MEMBERED RING SYSTEMS-PHOSPHORINANES.

Phosphorus n.m.r. spectral data on six-membered ring species is scarce, most of the information on the stereochemistry of these compounds being derived from proton and carbon n.m.r. spectral analysis and X-Ray diffraction studies.[5,8] From this work it has been established that the rings containing only one phosphorus atom have a distorted chair conformation,[36] with any substituents attached to

Table 1.3. : A variety of known cyclic polyorganophosphorus compounds and their phosphorus chemical shift positions.

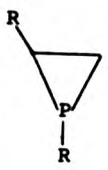
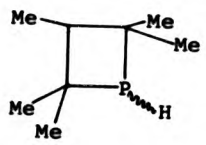
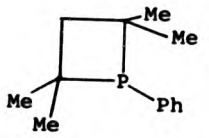
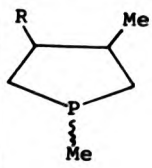
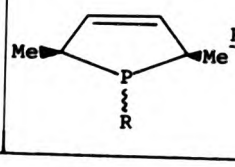
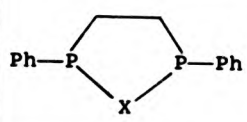
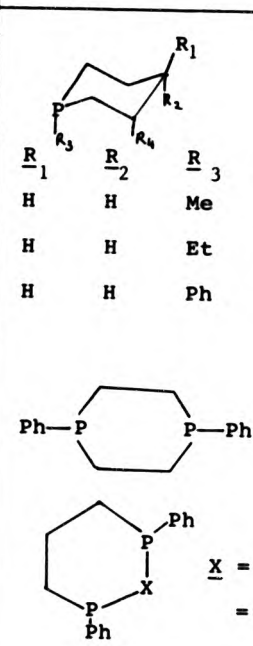
RING SIZE	COMPOUND	CHEMICAL SHIFT, δ, ppm.
3^{24}	 R = H H; Ph H	-341.0 -234.0
		cis, trans
	t-Bu(CH=CH$_2$)	-160.1, -171.0
	Ph(CH=CH$_2$)	-193.8, -204.3
32, 33, 39 4		+23.0
		+44.0, +49.0
34, 40 5	 R = H	cis, trans -33.4, -33.8
	R = Me	-41.6, -55.4
	 R = Ph	+15.1, +8.5

Table 1.3. Continued.

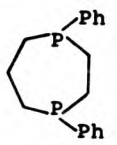
RING SIZE	COMPOUND	CHEMICAL SHIFT, δ, ppm
5 [35]	 X: CH_2; CMe_2	cis, trans: CH_2: -0.75, -1.51; CMe_2: +22.2, +17.7
6 [22,36,41]		(a) refers to position R_3

R_1	R_2	R_3	R_4	ax.(a)	eq.(a)
H	H	Me	H	-61.9	-55.7
H	H	Et	H	-39.7	-37.6
H	H	Ph	H	-38.9	-29.7

cis, -28.2; trans, -28.8

X = CH_2: cis, -33.5; trans, -34.5

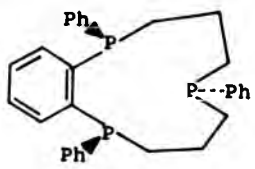
X = CMe_2: cis, -4.0; trans, -7.2

7 [22]		cis, -20.3; trans, -25.9
		-29.3, -30.2

the phosphorus atom in the axial position, and the lone pair of electrons equatorial. Although the phosphorus n.m.r. spectral data available are mainly confined to rings containing one phosphorus atom, some data are available for systems with two phosphorus atoms, namely the 1,4- and 1,5-diphosphorinanes (see Table 1.3.).

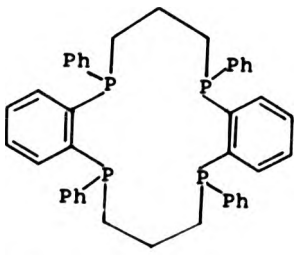
(d). LARGER RING SYSTEMS.

Larger rings containing three and four phosphorus atoms have been synthesised but their phosphorus n.m.r. spectral data are not reported, although their stereochemistry has been determined by X-Ray diffraction. However, two macrocyclic polyphosphorus compounds[37,38] which are analogues of crown ethers have been investigated by phosphorus n.m.r. spectroscopy in detail and are shown below in Figure 1.5.



δ(P) = +30.6ppm (s,2P)

δ(P) = +25.7ppm (s,1P)



δ(P) = +28.9ppm

Fig. 1.5. : Diagrammatic representation of two macrocyclic polyphosphorus systems.

Larger ring systems with sixteen to twenty atoms are known, but no phosphorus n.m.r. data are available.

COUPLING CONSTANTS-THEORETICAL CONSIDERATIONS.

The value of the coupling constant, J, provides information about the type of bonding present, but this is obscured by the contribution to the coupling constant, made by γ_A and γ_B (the nuclear magnetogyric ratios of atoms A and B). Thus in order to obtain correlations between the nature of the bonding system (i.e. the electronic environment) and spin-spin coupling, the reduced coupling constant, K_{AB}, is often used (Equation 1.2.).[42]

$$K_{AB} = \frac{4\pi^2 . J(AB)}{h \gamma_A . \gamma_B} \qquad \text{EQUATION 1.2.}$$

The coupling constant can be either positive or negative and the resonance frequency of one nucleus may be increased or decreased by a particular orientation of a coupled nucleus. The sign of the coupling constant is dependent upon the bonding system and the sign of the product $\gamma_A . \gamma_B$. For ^{31}P, ^{1}H and ^{13}C, the magnetic moment and the angular momentum have the same direction and hence γ is positive in each case.

The magnitude of the coupling constant for a particular pair of nuclei depends on the following factors:-[43]

(1). The magnetic moments of the two nuclei. These are directly proportional to the product $\gamma_A . \gamma_B$.

(2). The valence s-electron density at the nucleus,

which is described by the Fermi-contact term, is independent of the nuclear moments of A and B, and is dependent only upon the electronic enviroment. Following Ramsey, it can be shown that the reduced coupling constant K_{AB}, can be written in terms of three separate contributions (Equation 1.3).

$$K_{AB} = K^{1}_{AB_{ORBITAL}} + K^{2}_{AB_{SPIN-DIPOLAR}} + K^{3}_{AB_{SPIN-CONTACT}} \qquad \text{EQUATION 1.3.}$$

It is found that the spin contact term K^{3}_{AB} makes the most significant contribution to the spin-spin coupling of directly bonded atoms, since K^{3}_{AB} includes the terms involving the valence shell s-electrons on atoms A and B. This leads to a relationship between the coupling constant and the amount of s-electron character in hybridised orbitals on the atoms concerned. Since s-electrons have an appreciable electron density in the immediate nuclear enviroment they make a contribution to the coupling constant, unlike other types of electrons, which make no contribution to the contact term. However, only a small number of coupling constants are discussed in the current study, so the reduced coupling constant theory is not directly relevant.

The percentage of s-character for phosphorus containing molecules is determined by the hybridisation of the directly bonded P and X atoms. Often, sp^3 hybridised phosphorus atoms have larger values of J(P-X) than when the phosphorus atom uses only p -orbitals in bonding.

Thus, $^{1}J(P^{IV}-H)$ values for phosphorus cations such as $PH_{\underline{n}}R^{+}_{4-\underline{n}}$, where an $\underline{sp}^{3}$ bonding scheme predominates, are about 500Hz., whilst $^{1}J(P^{III}-H)$ values for phosphines such as $PH_{\underline{n}}R_{3-\underline{n}}$, with phosphorus bonding of high $\underline{p}$ - character are in the region of 200Hz. Furthermore, as the electronegativity of a bonded atom $\underline{X}$ increases, the percentage $\underline{s}$-character of the P-X bond increases,[44] making the coupling constant more positive.

THE MAGNITUDE OF $^{n}J(P^{III}-P^{III})$ COUPLING CONSTANTS.

Direct $^{1}J(P-P)$ coupling constants have been extensively reviewed by Finer and Harris;[45] work on these classes of compounds was outside the scope of the study and this section will deal with the magnitude of $^{n}J(P^{III}-P^{III})$ coupling constants (n = 2, 3 and 4), via carbon atoms which are $\underline{sp}^{2}$ and $\underline{sp}^{3}$ hybridised.

It has been found that the magnitude of $^{n}J(P-P)$ coupling is influenced by four main factors:

(1). The number of bonds between the two phosphorus atoms. Here, it is generally found that as the number of bonds increases, the magnitude of $^{n}J(P-P)$ decreases, a pertinent example being a series of the ditertiary diphosphines $Ph_2P(CH_2)_{\underline{n}}PPh_2$.[46] (Table 1.4.).

Table 1.4. : Magnitudes of $^{n}J(P^{III}-P^{III})$ in ditertiary diphosphines.

DITERTIARY DIPHOSPHINE	$^{n}J(P-P)$ Hz.
$Ph_2P(CH_2)_1PPh_2$	+125.0
$Ph_2P(CH_2)_2PPh_2$	+33.0
$Ph_2P(CH_2)_3PPh_2$	1.0

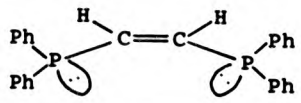
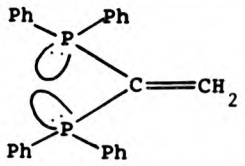
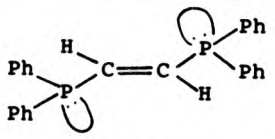
However, this rule is not invariably followed.

(2). The orientation of the phosphorus lone pair of electrons. It has been shown that conformations where the lone pairs on the two coupled phosphorus atoms are trans to each other are associated with low and possibily negative values of $^{n}J(P-P)$, whilst the cis conformation gives rise to large, positive values. Generally, steric effects lead to the predominance of the trans conformation when bulky R groups (alkyl or aryl) are present on the phosphorus atom. Table 1.5. gives a few examples of the lone-pair orientation effect.[46,47]

(3). The effective nuclear charge at the phosphorus (III) atom. This is found to increase with bonding to electronegative groups, but the changes in effective electronegativity induced by alkyl and aryl groups are minimal when compared to those produced by other groups or atoms such as chlorine.[17] Since all the ligands studied in this work

involve alkyl and aryl groups directly attached to the phosphorus atoms, the very small changes observed in the magnitude of ^{n}J(P-P) cannot be directly attributed to this factor.

Table 1.5.: Examples of the lone pair orientation effect for a variety of ditertiary diphosphines.

STRUCTURE		^{n}J(P-P)Hz
	'cis'	+105.5
	'cis'	+98.0
	'trans'	+13.0

(4). The hybridisation of the phosphorus (III) atom. As discussed previously, hybridisation for phosphorus (III) compounds is usually close to p^3 in character, with the non-bonding 3s pair of electrons playing only a minor role in the bonding pathway. However, in phosphorus (V) compounds an sp^3 hybridisation is approached, so the s-character of

the bonding orbitals used by the phosphorus atom increases and correspondingly enhances $^{n}J(P-P)$.[48] This point is relevant when considering P=S bonding in sulphurised species (Chapter 3).

Attachment of bulky substituents to the phosphorus (III) atom can lead to considerable distortions in bond angles and hence to changes in the hybridisation (i.e. a significant deviation from pure p^3 character). In general, the presence of such bulky groups tends to increase the bond angles and hence the s-character associated with the coupling pathway. However, the changes in the coupling constant actually observed are several orders of magnitude larger than those predicted by reasonable bond angle changes (Table 1.6.).[49]

These large variations in coupling constant are probably due to conformational changes, where the steric effects of bulky groups have to be considered, since it is already known (Factor 2) that the lone pair orientation may significantly influence $^{n}J(P-P)$.

Table 1.6. : $^{2}J(P-P)$ data for mixed ditertiary diphosphines.

MIXED DITERTIARY DIPHOSPHINES	$^{2}J(P-P)$ Hz.
$Ph_2P(CH_2)_2PMe_2$	108.0
$Ph_2P(CH_2)_2P(i\text{-}Pr)_2$	119.0
$Ph_2P(CH_2)_2P(t\text{-}Bu)_2$	138.0

In summary, a number of factors have to be considered when comparing the magnitudes of $^{n}J(P-P)$ coupling constants. The most important factors influencing the magnitude are the conformation of the molecule, with regard to the orientation of the lone pair of 3s electrons, in addition to the degree of s-character present along the coupling pathway. Conformational change criteria may apply equally to cyclic systems containing phosphorus (III) atoms, especially in larger rings where there is greater molecular flexibility.

$^{n}J(P^{III}-P^{III})$ COUPLING CONSTANTS OF CYCLIC AND POLYCYCLIC SYSTEMS.

In cyclic and polycyclic systems, the factors affecting the magnitude of the $^{n}J(P-P)$ coupling constant are the same as those for acyclic phosphorus compounds. However, the range of conformational possibilities may be restricted. Additionally, with these types of compounds, there may be several pathways connecting a pair of coupled phosphorus nuclei. It has been assumed, that the net coupling constant in cyclic systems is the algebraic sum of the couplings through the alternative bond pathways, as suggested by Grim et al[48] in their work on bidentate phosphorus ligands, cyclised through a metal atom. For example, in a five-membered ring system consisting of two phosphorus (III) atoms (Fig. 1.6) the $^{2}J(P-P)$ coupling discussed would in essence be a combination of

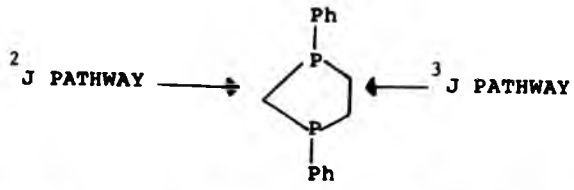


Fig. 1.6. : Pictorial representation of the ^{2}J(P-P) and ^{3}J(P-P) coupling pathways for 1,3-diphospholane.

^{2}J(P-P) and ^{3}J(P-P). Since ^{2}J and ^{3}J are commonly of opposite sign a decrease in magnitude may be observed in a five-membered ring when compared with the coupling constant in a comparable linear system.[50] However, in a six-membered ring the ^{2}J and ^{4}J couplings are usually of the same sign, thus a net increase in ^{2}J(P-P) would be expected compared to the corresponding acyclic system.

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CHAPTER 2.

NOVEL FIVE-MEMBERED CYCLIC ORGANOPHOSPHORUS COMPOUND AND RELATED POLYORGANOPHOSPHORUS COMPOUNDS.

INTRODUCTION.

The aim of this section of work was the synthesis of a range of new cyclic diphosphines based on 1,2-(monophenylphosphino)ethane as a backbone. The systems of greatest interest are the five-membered rings additionally possessing an alkene functional group, the presence of which would facilitate the introduction of additional organophosphorus groups, thus forming new polyphosphorus phosphines.

Five-membered ring systems possessing one phosphorus atom are known[1], but those with two or more phosphorus atoms are much rarer.[1,2] Stereochemical and n.m.r. spectroscopic data on such species are therefore quite limited.

This chapter is divided into two sections;

SECTION A discusses the synthesis and n.m.r. spectral analysis of a new five-membered cyclic organophosphine, (X).

SECTION B discusses the stereochemistry and n.m.r. spectral analysis of novel polyphosphorus phosphines derived from (X).

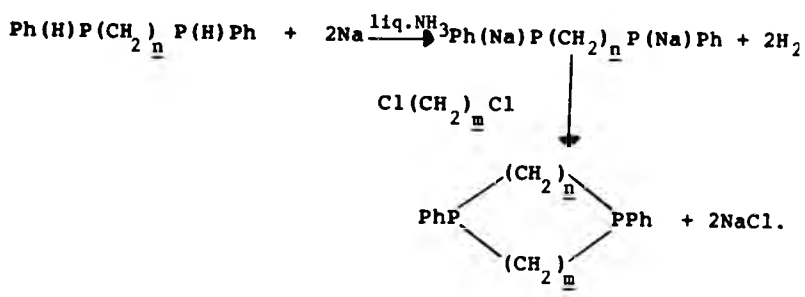
SECTION A.

NEW FIVE-MEMBERED CYCLIC ORGANOPHOSPHORUS COMPOUND (X).

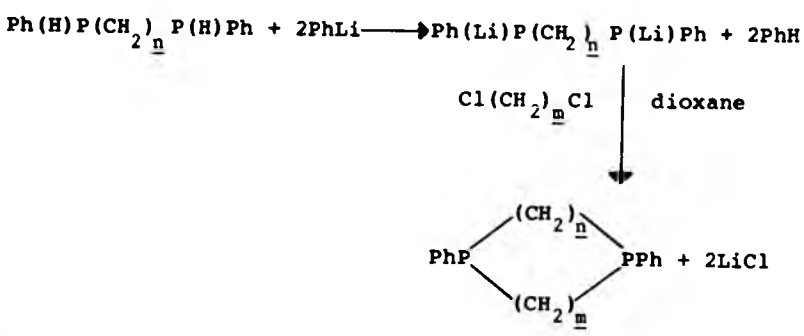
PREPARATION.

The known methods of preparation of cyclic diphosphines are based on Reactions (1) and (2): both are systems involving the synthesis of disecondary diphosphines by *metallation* of ditertiary diphosphines and subsequent reaction with an alkyl or aryl halide[3].

REACTION (1).



REACTION (2).



The current study has shown that the synthesis of disecondary diphosphines by the sodium/liquid ammonia method (Reaction (1)) where $\underline{n}$ = 1 or 2 produces mixtures; where $\underline{n}$ = 1 the ^{31}P n.m.r. spectrum indicates the presence of six phosphorus-containing moieties, whereas when $\underline{n}$ = 2, equal amounts of Ph_2PH and $Ph(H)P(CH_2)_2P(H)Ph$ are formed. In the current study cleavage of the phenyl group of dppe by lithium in THF at 0°C was found to be a much milder synthetic route resulting in good yields of the desired product, except where $\underline{n}$ = 1.

From this knowledge and from work conducted on lithiated disecondary diphosphines (see Chapter 4), a simpler and more convenient synthesis analogous to Reaction (2) was developed. In this a stoichiometric amount of the desired alkyl or aryl halide was added to the lithiated species of 1,2-(monophenylphosphino)ethane, in diethyl ether at 0° C (Reaction (3)).

REACTION (3).

$$Ph(H)P(CH_2)_2P(H)Ph + 2BuLi \xrightarrow[0°C]{Et_2O} \text{"}Ph(Li)P(CH_2)_2P(Li)Ph\text{"} + 2BuH$$

$$\text{"}Ph(Li)P(CH_2)_2P(Li)Ph\text{"} \xrightarrow{X(R)X} \underset{\text{PhP}}{\overset{(CH_2)_2}{\diagup\diagdown}}\underset{R}{\overset{}{\diagdown\diagup}}\text{PPh} + 2LiX$$

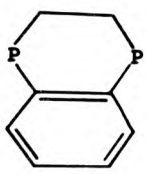
R = alkylene or arylene group.

X = halide Cl or F.

In order to test the viability of this reaction method, it was used to synthesise the two known cyclic diphosphines, 1,3-diphospholane and 1,4-diphosphorinane[4,5] (Fig. 2.1).

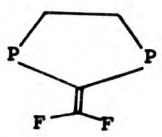
1,3-DIPHOSPHOLANE (I).

1,4-DIPHOSPHORINANE (II)

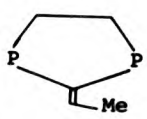


(III)

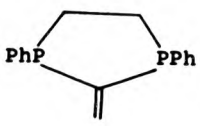
(IV)



(V)



(VI)



(X)

Fig. 2.1. : Examples of the variety of compounds whose syntheses were attempted by Reaction (3).

The ^{31}P n.m.r. spectra of the reaction solutions of these two compounds ((I) and (II)) indicated the presence of the desired products only, and these were isolated as white crystalline solids in good yields.

Consequently, the analogous preparations of the compounds (III) to (VI) and (X) was attempted, but were generally unsuccessful except for (X), which was prepared from 1,2-(monophenylphosphino)ethane and vinylidene dichloride.

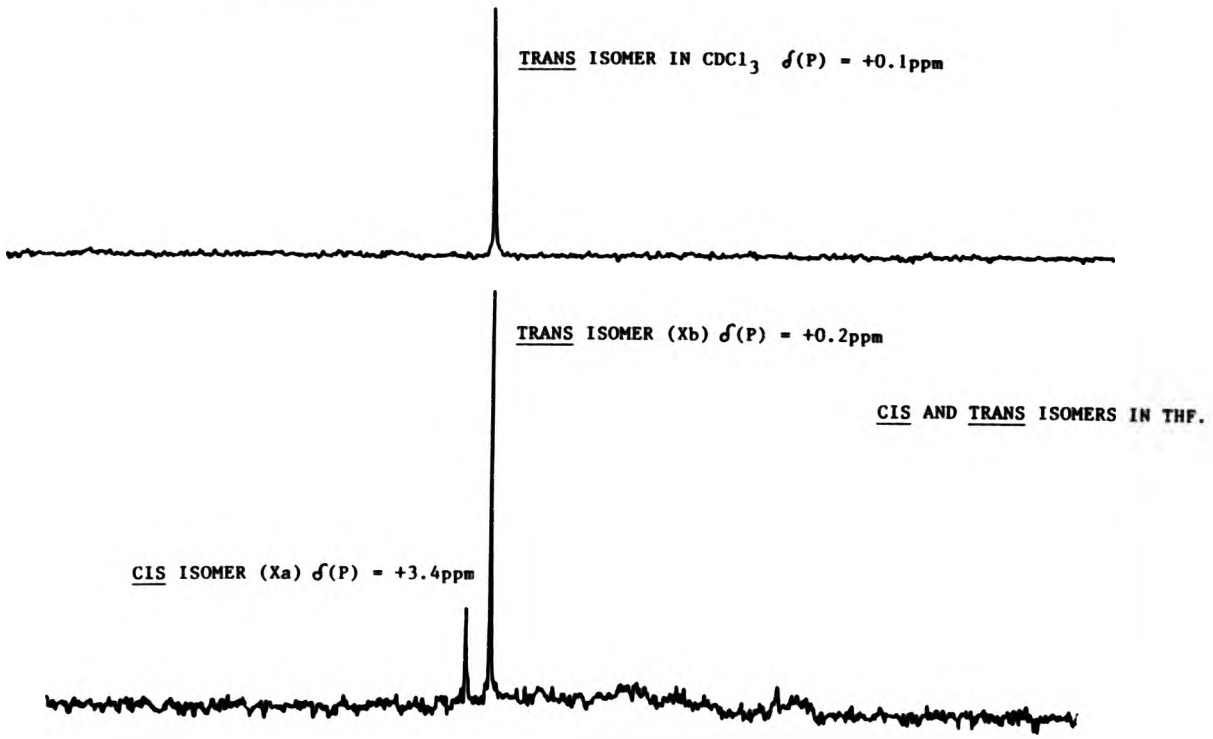
RESULTS AND DISCUSSION.

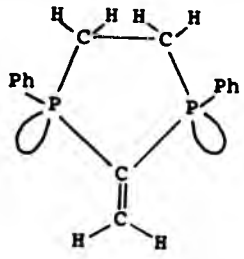
^{31}P N.M.R. SPECTRAL ANALYSIS OF THE CYCLIC DIPHOSPHINE (X).

The ^{31}P n.m.r. spectrum of the reaction solution reveals two singlet resonances at $\delta(P) = +3.4$ppm and $\delta(P) = -0.2$ppm, in an approximate ratio of 1:5 (Spectrum 2.1.). It can be surmised that these two resonances indicate the presence of two diastereoisomers of phosphine (X), since the asymmetry of the phosphorus atoms in $Ph(H)P(CH_2)_2P(H)Ph$ is retained in phosphine (X). Interaction between the two phosphorus atoms is possible as there is only a two bond separation.

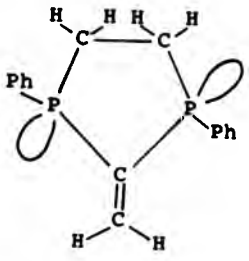
This diastereoisomerism can be visualised in terms of the orientation of the lone pairs within the ring system (Fig. 2.2), where only two configurations are possible, i.e. when the lone pairs are either cis (Xa) or trans (Xb) to each other.

Spectrum 2.1. : ^{31}P n.m.r. spectrum of the cyclic diphosphine (X), recorded at 36.2MHz.





(Xa) cis



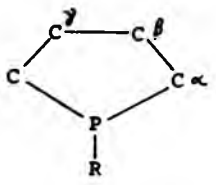
(Xb) trans

Fig. 2.2. : Diastereoisomers of the cyclic diphosphine (X) showing the orientation of the lone pairs of electrons.

Comparison of the phosphorus chemical shifts measured for the two isomers of ligand (X) with those of the phospholane systems (discussed in Chapter 1) suggests that the resonance at δ(P) = +3.4ppm arises from the cis isomer and that at δ(P) = -0.2ppm from the trans isomer.

The high frequency chemical shift values obtained for the isomers (Xa) and (Xb) relative to the phospholanes possessing one phosphorus atom (1-methylphospholane[6] δ(P) = -32.0ppm) indicate a shielding effect at the phosphorus nuclei. Breen et al[6] have used the Group Contribution (G.C.) concept to predict the phosphorus chemical shifts for various phospholanes and have observed a ring contribution of +11.0ppm. Their postulates are based upon the comparison of the five-membered phospholane ring with an analogous acyclic system consisting of two ethyl groups which has a total G.C. of +14.0ppm (detailed in Chapter 1.). This may be extended in the cyclic case by designating each of the

ring carbon atoms relative to the phosphorus atom (Fig. 2.3), to give a resultant G.C. of -10.0ppm.



G.C. = -21 + 14 βC - 3γC ppm

= -21 + 14 - 3

= -10ppm.

Fig. 2.3. : Labelling scheme for the ring carbon atoms of the phospholane systems with the G.C. calculations of the ring.

In applying the G.C. concept to phosphine (X) it must be remembered that there are two contributions made to the system:

(a) by the methylene backbone and
(b) by the vinyl group.

The vinyl and phenyl groups attached to the phosphorus atoms have an anisotropic deshielding effect, which would be expected to result in a high frequency shift. As the carbon atoms provide a positive contribution to the G.C. value, the presence of two such species in phosphine (X) gives a greater high frequency shift than in the phospholanes.

However, the expected anisotropic deshielding effect at the phosphorus atoms is not observed to any great extent. Thus a more relevant comparison would be between phosphine (X) and 1,3-diphospholane (Fig. 2.4).

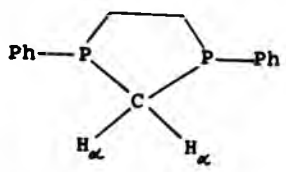


Fig. 2.4. : 1,3-diphospholane indicating the two ∝-protons involved in hyperconjugation.

1,3-diphospholane has two ∝-protons, which due to hyperconjugation (discussed in Chapter 1.), may be tentatively proposed to lead to shielding of the two phosphorus nuclei. This is reflected by the low frequency chemical shifts, of δ(P)cis = -0.7ppm and δ(P)trans = -1.5ppm.[2] This would then seem to imply that for phosphine (X), the ring structure possibly permits a significant electron distribution between the phosphorus atoms and the double bond. This would result in shielding of the phosphorus atoms, reflected by the chemical shifts of δ(P) = +3.4ppm and δ(P) = -0.2ppm.

It has only been possible to isolate one of the diastereoisomers in a yield of 30%, as an air-stable white crystalline solid, with a sharp melting point (see Experimental Chapter). The ^{31}P chemical shift in deuteriated chloroform is found to be +0.1ppm, which corresponds to the major diastereoisomer (the slight variation in the chemical shift position is presumably due to a solvent effect.). This isolated product is probably the trans isomer as

predicted from the known phosphorus chemical shifts of diphospholanes.

^{13}C N.M.R. SPECTRAL ANALYSIS OF THE ISOLATED DIASTEREOISOMER OF THE CYCLIC DIPHOSPHINE (X).

(i). THE PHENYL CARBON ATOMS.

The ^{13}C n.m.r. spectrum for each phenyl carbon atom revealed an AA'X spin system (see Appendix for description), where A, A' = phosphorus and X = phenyl carbon (see Fig. 2.5 for the labelling scheme and Spectrum 2.2.).

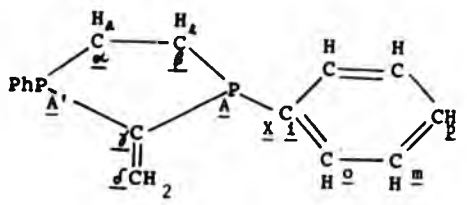
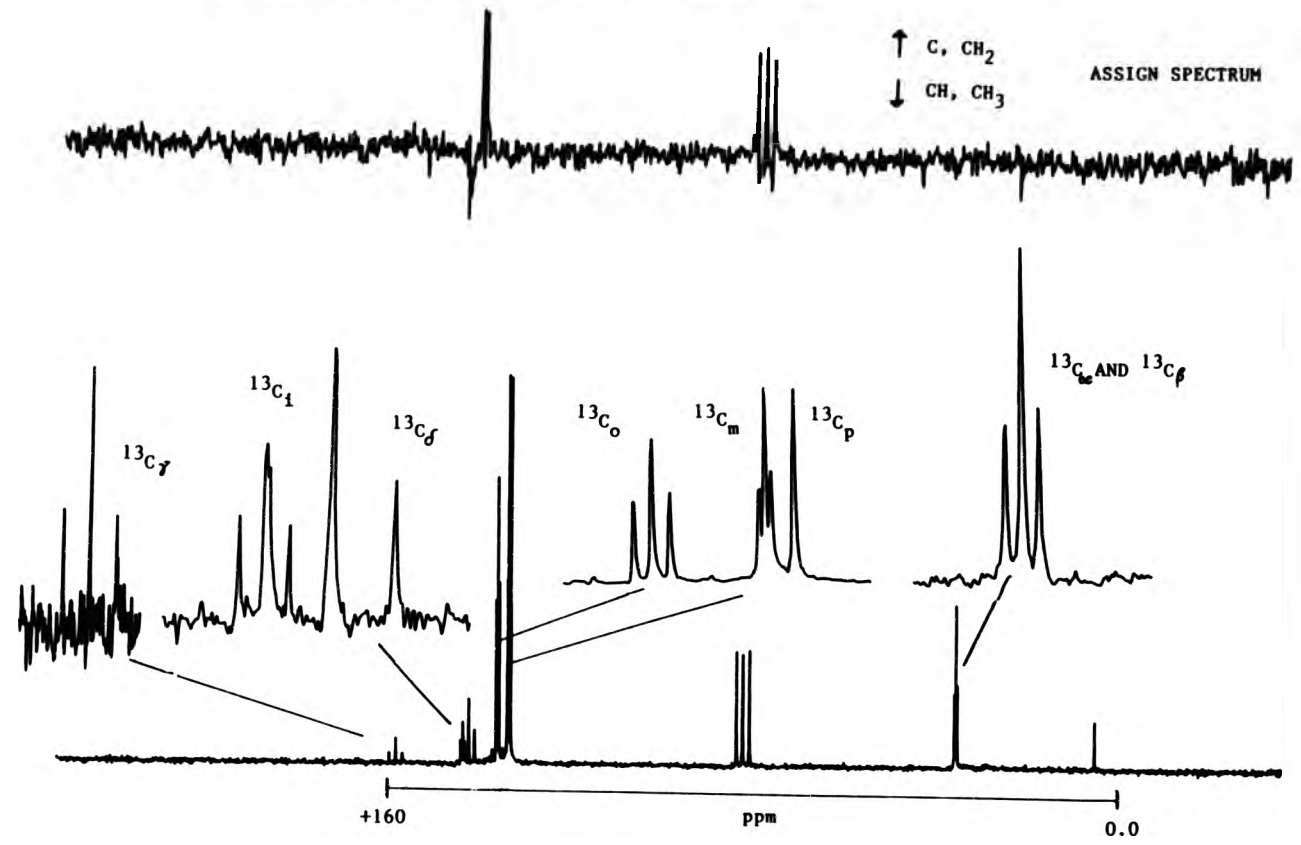


Fig. 2.5. : Labelling scheme for the carbon atoms of phosphine (X).

For the $^{13}C_{\underline{i}}$ and $^{13}C_{\underline{m}}$ carbon atoms only three of the expected five resonances are observed, with N = 22.7Hz and 5.8Hz respectively. The $^{13}C_{\underline{o}}$ carbon atoms are found to show all five resonances where N = 16.8Hz and s = 53.4Hz. If it is taken that $^{4}J(P_{A'}-{}^{13}C_{\underline{i}})$ is zero because it is a

Spectrum 2.2. : ^{13}C n.m.r. spectrum of the cyclic diphosphine (X), and assign spectrum, recorded at 22.5MHz.



long range coupling, then N = L = 16.8Hz and the magnitude of $^{2}J(P_{A}-P_{A'})$ can be calculated using the relationship

$$^{2}J(P_{A}-P_{A'}) = \sqrt{\frac{(s^{2} - L^{2})}{4}}$$

to give a value for $^{2}J(P_{A}-P_{A'})$ of 25.4Hz.

The magnitude of $^{2}J(P_{A}-P_{A'})$ here is small and indicates that the lone pairs on the phosphorus atoms in this system are <u>trans</u> to each other, since it is known that the magnitude of the $^{2}J(P_{A}-P_{A'})$ is sensitive to the molecular conformation and configuration of the system (detailed in Chapter 1.).

The $^{13}C_{\underline{P}}$ carbons are observed as a singlet resonance at $\delta(^{13}C)$ = +128.4ppm and, since it can be assumed that the long range coupling of $^{6}J(P_{A'}-^{13}C_{\underline{P}})$ is zero, it follows that $^{4}J(P_{A}-^{13}C_{\underline{P}})$ is also zero.

<u>(ii). THE METHYLENE CARBON ATOMS.</u>

Each of the methylene $^{13}C_{\alpha}$ and $^{13}C_{\beta}$ carbon atoms shows only three of the five resonances of an AA'X spin system, with N = 14.6Hz.

(iii). THE ETHENE CARBON ATOMS.

Each of the ethene carbon atoms, $^{13}C_{\gamma}$ and $^{13}C_{\delta}$, is found to give a first order A_2X spin system, where A = phosphorus atoms which are magnetically and chemically equivalent and, X = $^{13}C_{\gamma}$ and $^{13}C_{\delta}$ carbon atoms. The predicted ^{13}C n.m.r. spectrum should consist of two symmetrical 1:2:1 triplets. These carbon resonances were assigned on the basis of the intensities of the resonances observed for the two triplets where, because of Nuclear Overhauser Effects, the intensity of the $^{13}C_{\delta}$ carbon atom bearing two protons would be predicted to be greater, whilst the intensity of quaternary $^{13}C_{\gamma}$ carbon atom resonances remain unaltered. Such effects are observed for the $^{13}C_{\gamma}$ and $^{13}C_{\delta}$ resonances. In order to assign the two ethene carbon atoms unequivocally an ASSIGN experiment was conducted (Spectrum 2.2.), which confirmed these assumptions.

The n.m.r. parameters found from the analysis of the ^{13}C n.m.r. spectrum of phosphine (X) are tabulated in Table 2.1.

Table 2.1. : ^{13}C n.m.r. data for the cyclic diphosphine (X).

CHEMICAL SHIFT, δ, ppm.							
$^{13}C_{\underline{i}}$	$^{13}C_{\underline{o}}$	$^{13}C_{\underline{m}}$	$^{13}C_{\underline{p}}$	$^{13}C_{\alpha}$	$^{13}C_{\beta}$	$^{13}C_{\gamma}$	$^{13}C_{\delta}$
138.7	131.3	129.0	128.4	31.2	31.2	153.2	137.4

COUPLING CONSTANT, Hz.							
N						J	
$^{13}C_{\underline{i}}$	$^{13}C_{\underline{o}}$	$^{13}C_{\underline{m}}$	$^{13}C_{\underline{p}}$	$^{13}C_{\alpha}$	$^{13}C_{\beta}$	$^{1}J(P_A - {}^{13}C_{\gamma})$	$^{2}J(P_A - {}^{13}C_{\delta})$
22.7	16.9	5.9	-	14.7	14.7	33.0	27.8

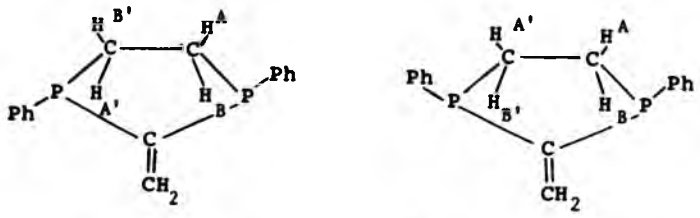
Note.

(a). Chemical shifts relative to internal $\delta(CDCl_3)$ = 77.7ppm.

(b). In $CDCl_3$ at 25°C.

^{1}H N.M.R. SPECTRAL ANALYSIS OF THE CYCLIC DIPHOSPHINE (X).

The phosphorus coupled ^{1}H n.m.r. spectrum showed extensive overlapping of the resonances. Thus, in order to simplify the spectrum a phosphorus decoupled ^{1}H n.m.r. spectrum was obtained, which revealed the methylene protons to describe a second order AA'BB'spin system (see Spectrum 2.3. and Fig. 2.6 for the labelling scheme).

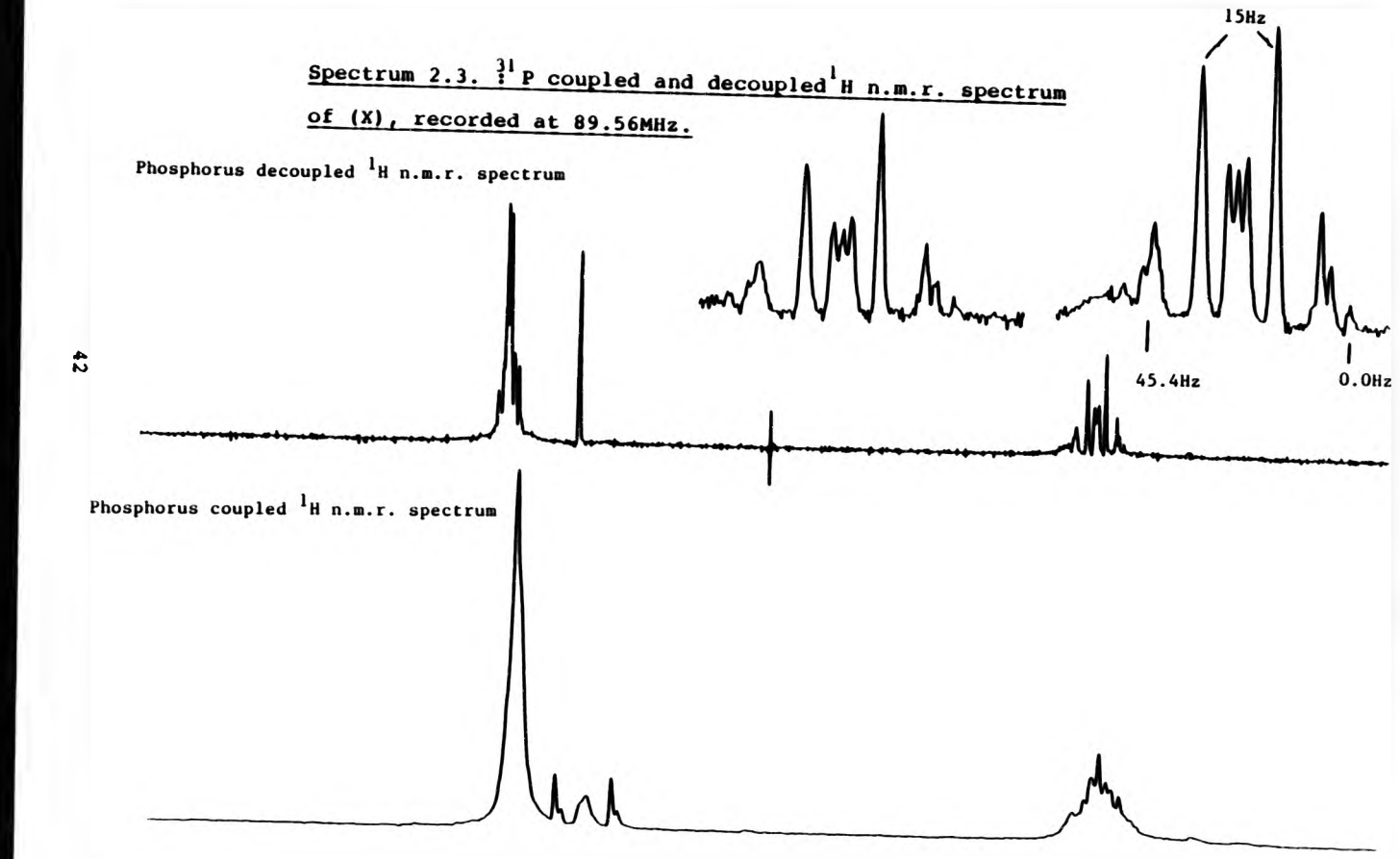


LIGAND (X).

Fig. 2.6. : Labelling scheme for the protons of the trans and cis isomers of (X).

Theoretically, ten resonances should be observed for the AA' and BB' parts of the spectrum, of which only nine resonances are found in the spectrum obtained. Since all the resonances are not resolved, it is not possible to evaluate the n.m.r. parameters for a complete analysis of the ^{1}H n.m.r. spectrum. However, the four methylene protons for each isomer would both be expected to be described by an AA'BB'spin system, thus determination of the isomer isolated would not be possible by ^{1}H n.m.r. spectroscopy.

However, it will be shown from the product of the addition of Ph_2PH to this molecule that the lone pairs are actually trans to each other.



Spectrum 2.3. $^{31}_{\frac{1}{2}}P$ coupled and decoupled ^{1}H n.m.r. spectrum of (X), recorded at 89.56MHz.

SECTION B.

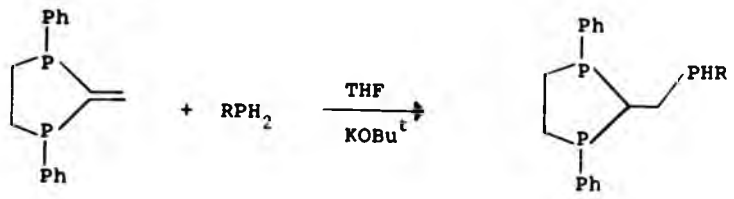
POLYORGANOPHOSPHORUS COMPOUNDS.

(A). TRIPHOSPHINES.

PREPARATION.

The triphosphines have been synthesised from a variety of primary and secondary phosphines. To a solution of (Xb) in THF was added an equimolar amount of the desired phosphine, together with a catalytic quantity of potassium tertiary butoxide[7]. This resulted in the complete formation of the required triphosphine (Equations 2.1. and 2.2.).

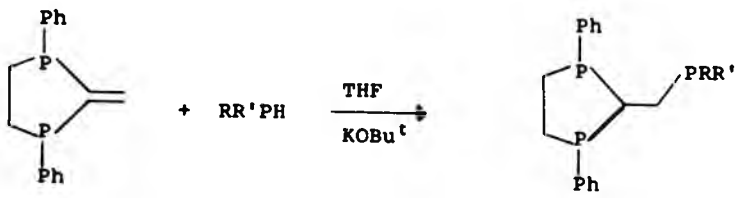
EQUATION 2.1.



R = Ph (VII).

R = $C_6H_2((C(CH_3)_3)_3$ (VIII).

EQUATION 2.2.



R,R' = Ph_2 (IX).

R,R' = (n-Bu)Ph (XI).

THE ^{31}P N.M.R. SPECTRAL ANALYSIS OF THE TRIPHOSPHINES.

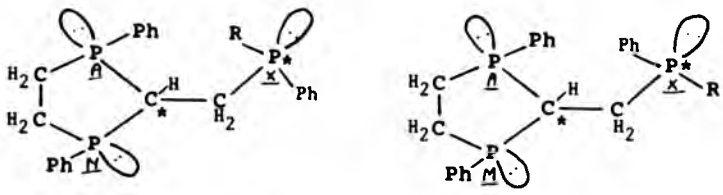
The analysis of the ^{31}P n.m.r. spectra of compounds (VII) to (IX) and (XI), shows that all give first order AMX spin systems, thus allowing the direct measurement of the three chemical shift positions $\delta(P_A)$, $\delta(P_M)$, and $\delta(P_X)$; and the three coupling constants $^2J(P_A\text{-}P_M)$, $^3J(P_A\text{-}P_X)$ and $^3J(P_M\text{-}P_X)$.

In the triphosphines (VII) to (IX) and (XI), all three phosphorus atoms are tricoordinated and in all cases the two ring phosphorus atoms are tertiary. However, for compounds (VII) and (VIII), the exocyclic phosphorus atom is secondary, whereas for (IX) and (XI) it is again tertiary.

The presence of a first order AMX spin system reveals that the two phosphorus nuclei in the ring system are magnetically and chemically inequivalent. The low magnitude of $^2J(P_A\text{-}P_M)$ [12.0Hz to 13.0Hz] would seem to suggest that the lone pairs of electrons of the two ring phosphorus atoms are <u>trans</u> to each other. A <u>cis</u> relationship would be expected to give rise to large values (i.e. >100Hz) for the $^2J(P_A\text{-}P_M)$ (discussed in Chapter 1). Thus it is the <u>trans</u> isomer (Xb) which has been isolated of compound (X).

The above conclusions are confirmed by the presence of two diastereoisomers for each of the triphosphines (VII), (VIII) and (XI). These three compounds possess a true chiral carbon atom and a prochiral P_X centre (Fig. 2.7). It is now relevant to give a brief description of prochirality.

A tetrahedral atom linked to two ligands and two



R = H or n-Bu

Fig. 2.7. : Diagram showing the two diastereoisomers of compounds (VII), (VIII) and (XI), possessing chiral P_A and P_X centres (asterisk); and the AMX spin system labelling scheme.

other different ligands (^{31}Paabc) is said to be prochiral. If one of the a ligands is replaced by another ligand different from any of the others then a new chiral centre has been produced (^{31}Pabcd). The two identical ligands attached to a prochiral centre are said to be enantiopic if their separate replacement by a group different from any attached to the prochiral centre gives rise to a pair of enantiomers; and are said to be diasteretopic if diastereoisomers are obtained upon such replacement.

The prochiral P_X atom in conjunction with the two inequivalent ring phosphorus atoms allows the formation of diastereoisomers. If the ring phosphorus lone pairs had been in a cis conformation, then an A_2X spin system would have been expected for the triphosphines.

Triphosphine (IX) also possesses one chiral carbon centre. The ^{31}P n.m.r. spectrum indicates the presence of only one form of (IX) which results from the achirality

of the P_X atom, and from free rotation about the single carbon-carbon and carbon-phosphorus bonds, sterically permitting the formation of only one configuration (Fig. 2.8).

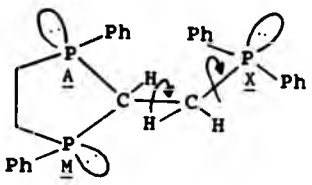


Fig. 2.8. : Phosphorus atom labelling scheme for compound (IX) and showing the free rotation about the carbon-carbon and carbon-phosphorus bonds.

The assignment of the two sets of n.m.r. parameters (the relative chemical shift positions and coupling constants), was made in the following manner.

In compounds (VII) and (VIII), one proton is directly bonded to the exocyclic P_X atom, a fact confirmed by an off-resonance ^1H-decoupling experiment. Results from this experiment indicate that the set of resonances in the low frequency region (δ(Compound (VII)) = -50.2ppm and δ(Compound (VIII)) = -68.6ppm) arise from the P_X nuclei. Therefore, the two sets of resonances in the high frequency region of the spectrum are taken to arise from the P_A and P_M nuclei. Similarly, for compounds (IX) and (XI), the set of resonances in the low frequency region are assigned to the exocyclic P_X nucleus.

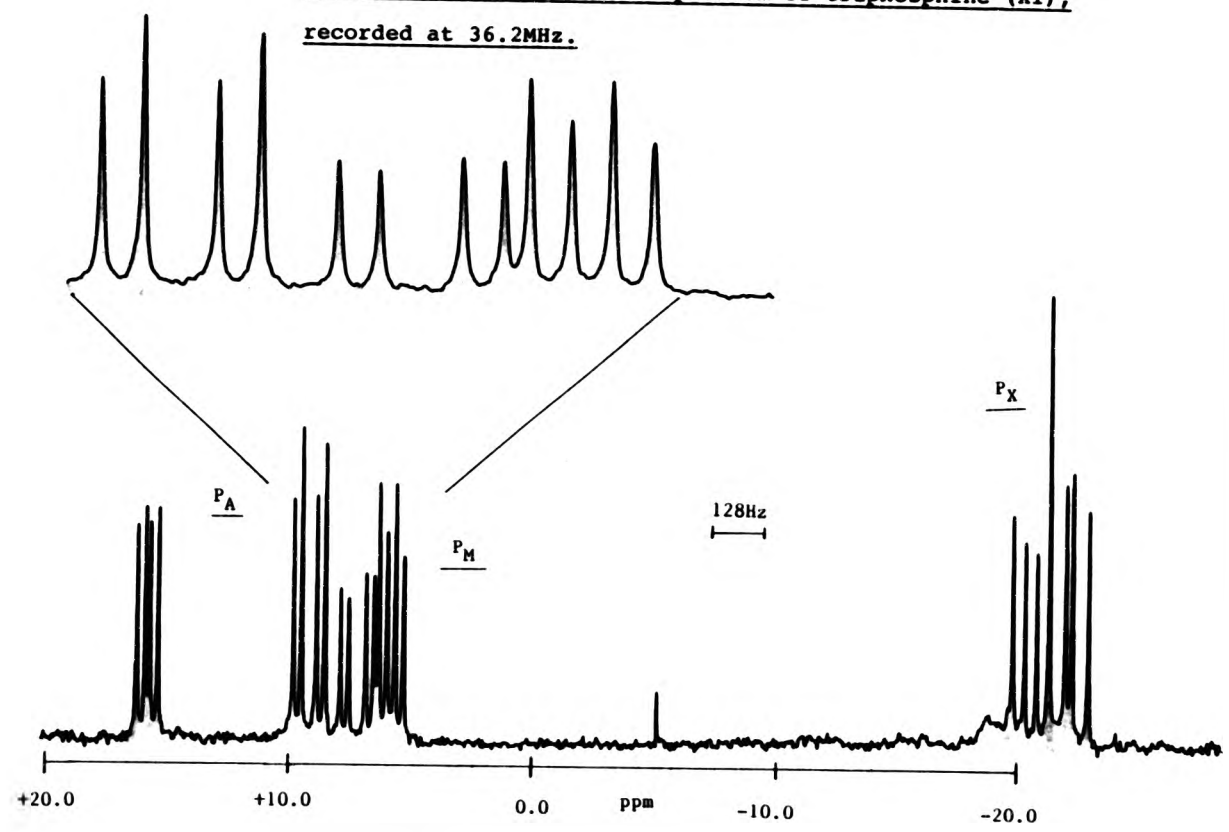
The route taken in the analysis of the ^{31}P n.m.r. spectra of compounds (VII), (VIII) and (XI) is described using (XI) as a detailed example. Triphosphine (IX) is described separately later in this section.

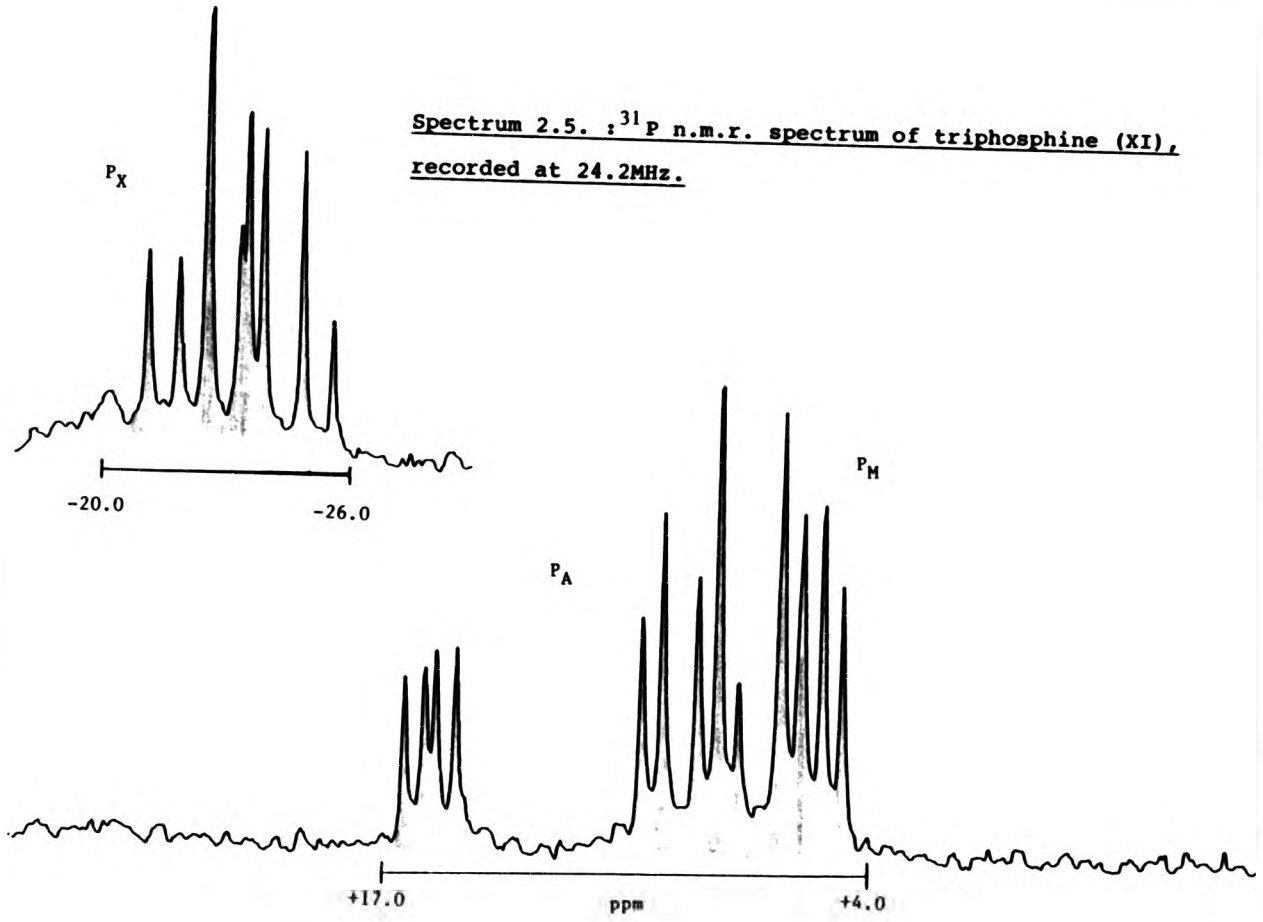
The ^{31}P n.m.r. spectrum of (XI), obtained at 36.2MHz consists of twenty-four lines, one pair of which overlap so that twenty-three lines are observed (Spectrum 2.4.). A first order AMX spin system gives rise to twelve resonances so this indicates the presence of two diastereoisomers, in approximately the ratio of 1:2 (the two diastereoisomers of (VII) and (VIII) were present in approximately equal proportions). Since no second-order coupling is observed, the distortions of the intensities of the resonances possibily result from the pulse rate used. This will be discussed later.

At 24.2MHz, twenty-two resonances are observed, i.e. two pairs overlap (Spectrum 2.5.). The repeated splittings of 12.8Hz (resonances 1-2, 2-3, 8-9, and 10-12) and 13.1Hz (resonances 5-6, 7-8, 11-13, and 14-15) found in the high frequency region, are taken to be coupling constants, as they are also observed in the spectrum obtained at 36.2MHz. They probably originate from the couplings between the P_A and P_M nuclei.

Thus, from the ^{31}P n.m.r. spectrum obtained at 36.2MHz, resonances 1 to 4 and 9 to 12, where $J(P\text{-}P) = 12.8Hz$, can be assigned to one diastereoisomer (XIa)/(green); and resonances 5 to 8 and 13 to 16, where $^{n}J(P\text{-}P)=13.1Hz$ to diastereoisomer (XIb)/(red); $n = 2$ or 3 (see Spectrum 2.4. for the colouring scheme.).

Spectrum 2.4. : ^{31}P n.m.r. spectrum of triphosphine (XI), recorded at 36.2MHz.





Spectrum 2.5. : ^{31}P n.m.r. spectrum of triphosphine (XI), recorded at 24.2MHz.

The larger splittings at 24.2MHz of 19.8Hz (resonances 1-3 and 2-4); 36.2Hz (resonances 8-10 and 9-12); and 25.9Hz (resonances 11-14 and 13-15) in the high frequency regions, are also observed in the 36.2MHz spectrum and are thus taken to be coupling constants. These couplings are also repeated in the P_X part of the spectrum and are observed both in the 24.2MHz and 36.2MHz spectra. It can then be assumed that these couplings arise from $^3J(P_A-P_X)$ and $^3J(P_M-P_X)$; with the 19.8Hz and 38.7Hz splittings originating from diastereoisomer (XIa)/(green) and that the 36.3Hz and 25.9Hz splittings originate from diastereoisomer (XIb)/(red).

The smaller coupling constants observed in the high frequency regions can be assigned as $^2J(P_A-P_M)_{(XIa)} = 12.8Hz$ and $^2J(P_A-P_M)_{(XIb)} = 13.1Hz$. The larger coupling constants can be assigned as $^3J(P_A-P_X)_{(XIa)} = 19.8Hz$, $^3J(P_M-P_X)_{(XIa)} = 38.7Hz$, $^3J(P_A-P_X)_{(XIb)} = 36.3Hz$ and $^3J(P_M-P_X)_{(XIb)} = 25.9Hz$.

The measurable parameters found from the analysis of the triphosphine ^{31}P n.m.r. spectra are presented in Table 2.2.

With respect to the relative chemical shifts, it is observed that the resonances from each type of phosphorus nucleus appear within specific, mutually exclusive regions.

The resonances from the P_A and P_M nuclei are observed in the high frequency spectral region; the P_A resonances being at a higher chemical shift than the P_M resonances ($\delta(P_A)$ = +9.0ppm to +16.0ppm and $\delta(P_M)$ = +5.5ppm to +7.0ppm). The high frequency phosphorus chemical shifts obtained for the two ring phosphorus atoms indicate, in the first

Table 2.2.: ^{31}P n.m.r. data for the triphosphines (VII), (VIII) and (XI).

COMPOUND	CHEMICAL SHIFT, δ, ppm.		
	($^{31}P_A$)	($^{31}P_M$)	($^{31}P_X$)
(VIIa)	+11.4	+6.7	-50.2
(VIIb)	+9.9	+5.9	-50.4
(VIIIa)	+13.1	+5.4	-68.2
(VIIIb)	+10.8	+5.8	-69.1
(XIa)	+15.8	+7.0	-22.2
(XIb)	+9.1	+5.6	-23.1

LIGAND	COUPLING CONSTANT, J , Hz.		
	$^2J(^{31}P_A - ^{31}P_M)$	$^3J(^{31}P_A - ^{31}P_X)$	$^3J(^{31}P_M - ^{31}P_X)$
(VIIa)	12.2	16.5	26.2
(VIIb)	12.2	19.5	26.9
(VIIIa)	11.0	26.9	36.6
(VIIIb)	11.0	54.3	21.4
(XIa)	12.8	19.8	38.7
(XIb)	13.1	36.3	25.9

NOTE.

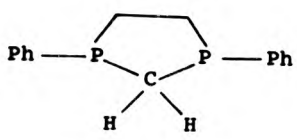
(a). Chemical shifts relative to external 85% H_3PO_4

(b). In THF/C_6D_6 at 25°C.

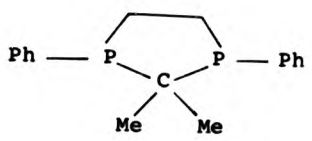
instance, a deshielding effect. The loss of the vinyl $-CH=CH_2$ fragment from the parent compound (XIb) by addition of a phosphine leads to further deshielding of the phosphorus ring nuclei. This may reflect conformational changes occurring to the phosphorus-carbon-phosphorus bond (Fig. 2.9 (2c)), as a result of steric effects upon replacement of the $-CH=CH_2$ group by the bulkier $-CH_2PR_2$ (or $-CH_2HR$) moiety.

In order to explain the high frequency shifts observed for the two ring phosphorus atoms, the tritertiary cyclic phosphines are compared to two known systems, whose phosphorus chemical shifts have been reported (Fig. 2.9 (2a and 2b)).[2]

It is reasonable to assume that in each of the systems (2a-c), the common methylene backbone unit contributes to the relevant phosphorus chemical shift values. Thus comparison of these three systems can be envisaged in terms of α-proton substitution. Diphospholane (2a) possesses two α-protons which, due to hyperconjugation, leads to shielding of the phosphorus nuclei, reflecting a low frequency value for the phosphorus chemical shift. However in diphospholane (2b), the two α-protons are substituted by two methyl groups resulting in the loss of hyperconjugation and consequently, loss of the shielding effect. Thus in comparison, the phosphorus chemical shift values are shifted to high frequency. The inductive effect,a low frequency shift expected from the two methyl groups is not observed. This may be due to (i) steric interaction between the methyl and phenyl moieties and, (ii) the fact that the exact nature of the methylene backbone contribution



(2a)



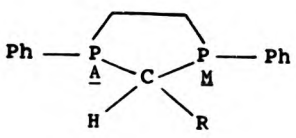
(2b)

(P)cis = -0.7ppm.

(P)trans = -1.5ppm.

(P)cis = +22.2ppm.

(P)trans = +17.7ppm.



(2c)

R = $-CH_2PR'_2$.

R = $-CH_2PHR'$.

(P_A)trans = +9.1ppm to +15.8ppm.

(P_M)trans = +5.4ppm to +7.0ppm.

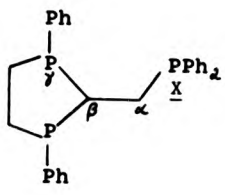
Fig. 2.9. : Comparison of the phosphorus chemical shifts of the two known diphospholanes (2a and 2b) and the novel tritertiary phosphines (VII), (VIII), (IX) and (XI).

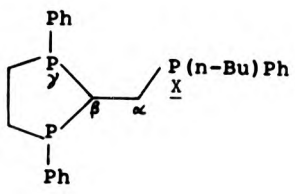
to the phosphorus shifts in a cyclic system is not known.

The tritertiary cyclic phosphine (2c) can be considered as showing only partial α-proton substitution as only one α-proton is substituted. This leads to a loss of hyperconjugation (relative to 2a) and to deshielding, though of a lower magnitude relative to 2b. Unfortunately no literature data are available for an analogous system, where there is substitution of only one α-proton by a methyl group. Such data would possibily permit determination of the methylene backbone contribution to the phosphorus chemical shifts and a subsequent empirical determination of the effect of the various α-carbon substiuents.

The difference between the two ring phosphorus chemical shifts in (2c) not only indicates that the two phosphorus atoms are inequivalent, but additionally reflects the average relative conformational relationship between each of the phosphorus atoms and the R group on the α-carbon atom. Thus, when the R group and the phenyl group are cis to each other, they would be expected to show greater high frequency shifts, due to steric effects.

The phosphorus chemical shifts obtained for the exocyclic P_X atom reflects the secondary (phosphines (VII) and (VIII)) and tertiary (phosphines (IX) and (XI)) natures of these atoms. The phosphorus chemical shift range in which the two classes of phosphines are found compares favourably with those for known analogous acyclic phosphines. Additionally, this can be confirmed by using the group contribution (G.C.) concept in calculating the expected phosphorus chemical shift, as shown in Fig. 2.10.





(IX) (XI)

G.C. = -21 + 14 βC - 3 γC ppm.

G.C. for Ph = -3ppm and n-Bu = -11ppm.

Thus for (IX),	AND	(XI),
G.C. = -16.0ppm		G.C. = -24.0ppm
i.e. $\delta(P_X)$ = -16.0ppm		$\delta(P_X)$ = -24.0ppm

The actual values measured are:

$\delta(P_X)$ = -15.9ppm	$\delta(P_X)$ = -22.2ppm and -23.1ppm (average -22.6ppm)

Fig. 2.10. : Group contribution calculations for the tritertiary phosphines (IX) and (XI).

NOTE

The G.C. method works if the ring phosphorus atom is taken to be equivalent to a carbon atom in the G.C. equation.

The magnitudes of $^{2}J(P-P)$ coupling constants measured for the tritertiary ligands are all similar (12.0Hz to 13.0Hz). This may indicate that the coupling between the ring phosphorus atoms is not significantly affected by the substituents on the exocyclic P_X atom.

The observed differences in the magnitudes of $^{3}J(P-P)$ coupling constants between each diastereoisomeric pair, could result from rotation about the carbon-carbon and carbon-phosphorus bonds, giving an average value for the two $^{3}J(P-P)$ coupling constants. More significantly, as a result of the free rotation about the carbon-carbon and carbon-phosphorus bonds, the energetically preferred conformation must dominate for each diastereoisomer.

THE ^{31}P N.M.R. SPECTRAL ANALYSIS OF TRIPHOSPHINE (IX).

The ^{31}P n.m.r. spectrum of triphosphine (IX) consists of eleven of the twelve resonances expected for a first order AMX spin system. One pair of resonances overlap in the P_X region giving rise to a deceptively 'simple triplet', as $^{3}J(P_A-P_X) = {}^{3}J(P_M-P_X) = 33.6Hz$ (Spectrum 2.6.). This spectrum was analysed in a similar manner to those for the other triphosphines described previously. The n.m.r. parameters are presented in Table 2.3.

Table 2.3. : ^{31}P n.m.r. data for triphosphine (IX).

CHEMICAL SHIFT, δ, ppm			COUPLING CONSTANT, J , Hz.		
P_A	P_M	P_X	$^2J(P_A-P_M)$	$^3J(P_A-P_X)$	$^3J(P_M-P_X)$
+10.3	+5.8	-15.9	12.8	33.6	33.6

NOTE

(a). Chemical shifts relative to external 85% H_3PO_4

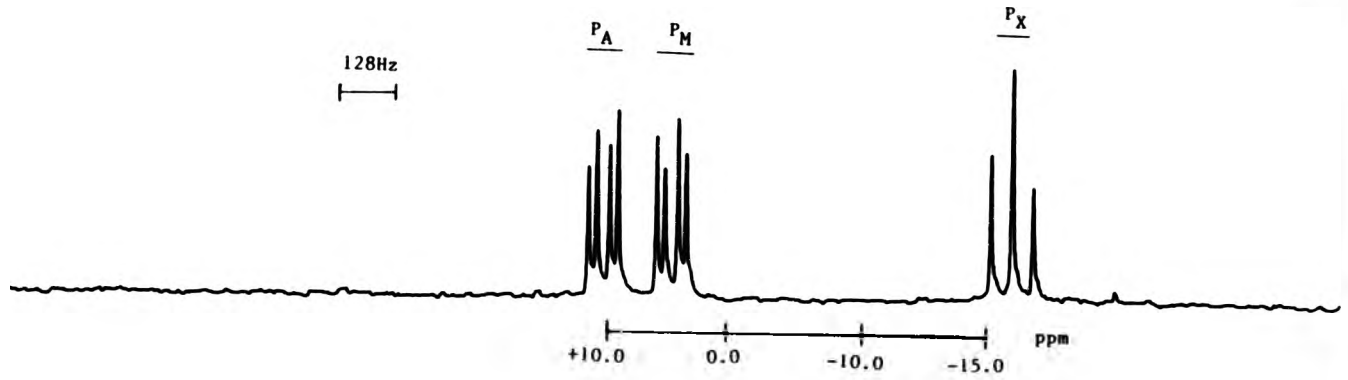
(b). In THF/C_6D_6 at 25°C.

DETERMINATION OF THE RELATIVE SIGNS OF COUPLING CONSTANTS BY SPIN-TICKLING.

A spin-tickling experiment[8] has been conducted to measure the relative signs of the coupling constants $^2J(P_A-P_M)$, $^3J(P_A-P_X)$ and $^3J(P_M-P_X)$, in triphosphine (IX). This triphosphine was used in this experiment as it is present in one form only; it gives a first order AMX spin system and all the chemical shift positions and coupling constants are readily measured. The AMX spin system consists of three subspectra which are well spaced due to weak coupling between the phosphorus nuclei and allows for perturbed resonances due to spin-tickling to be readily observed.

The sign and magnitude of a coupling constant are a measure of the extent to which the spin orientation of one

Spectrum 2.6 : ^{31}P n.m.r. spectrum of triphosphine (IX), recorded at 36.2MHz.



nucleus affects that of another, via the molecular electrons. This interaction is said to be positive when the energy of a nuclear spin is lowered by a second nucleus with antiparallel spin, and negative when lowered by a second nucleus with a parallel spin.

SPIN-TICKLING (DOUBLE RESONANCE) EXPERIMENT.

Spin-tickling experiments involve weak irradiation of one resonance of the spectrum (in the case of triphosphine (IX), a resonance in a multiplet arising from P_A, P_M or P_X) and observing the changes caused to other associated resonances of the spectrum. These changes are produced by the low-intensity (weak) radiofrequency energy applied in this double-resonance experiment, perturbing the spins without causing complete decoupling. The relevant effects of this type of selective irradiation are:

(a) that all connected transitions will be split into doublets;

(b) the doublet splitting is proportional to the square root of the intensity of the irradiated resonance and the magnitude B_2 of the irradiation field.

The irradiating field strength is usually expressed as $\gamma B_2/2\pi$, where γ is the magnetogyric ratio of the nucleus (for triphosphine (IX), ^{31}P nucleus = $+10.829 \times 10^7$ rad T^{-1} s^{-1}) irradiated and B_2 is the magnitude of the irradiating field, and then has units of Hz. When single resonances in spin multiplets are selectively irradiated, $\gamma B_2/2\pi$ may be in the order of one hertz or less.

To illustrate a spin-tickling experiment, a first order AMX spin system is considered, which is shown in a schematic form in Figure 2.11.

The spin-tickling experiments conducted produced two simultaneous experimental results, since the effect on two other phosphorus nuclei, associated with a particular transition of the irradiated resonance was observed.

Figure 2.13 represents the schematic form of the spectrum indicating the number scheme for each resonance, with the results tabulated in Table 2.4.

In order to determine the signs of the coupling constants, it was not necessary to conduct all five spin-tickling experiments shown in Table 2.4.; the full details could be evaluated from experiments (i), (iii) and (iv) alone and these are detailed below. However, all five experiments were performed for completeness and for confirmation reasons.

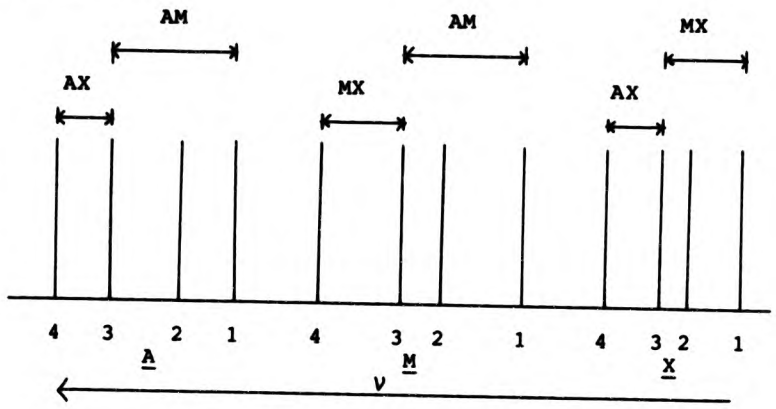
EXPERIMENT (i): When resonance A4 in the high frequency region is irradiated,

(a). the association of P_A and P_M with a particular spin state of P_X may be considered, comparing $^3J(P_A-P_X)$ and $^3J(P_M-P_X)$.

In the M part of the spectrum, resonances M4 and M3 also in the high frequency region are perturbed; the relative signs of $^3J(P_A-P_X)$ and $^3J(P_M-P_X)$ are the same.

(b). The association of P_A and P_X with a particular spin state of P_M may be considered, comparing $^2J(P_A-P_M)$ and $^3J(P_M-P_X)$.

Fig. 2.11.



All nuclei have I = 1/2 and γ is positive.

(a). J(AM), J(AX), J(MX) all positive.

A						+		+	−		−	+		−	+
M	+		+		−		−					+		+	−	−
X	+		−		+		−		+		−					

(b). J(AM) = positive, J(AX), J(MX) = negative

A						+		+	−		−	−		+	−	+
M	+		+		−		−					−		−	+	+
X	−		+		−		+		−		+					

(c). J(AM), J(AX) = positive, J(MX) = negative

A						+		−	+		−	+		+	−	−
M	+		−		+		−					−		+	−	+
X	+		+		−		−		−		+					

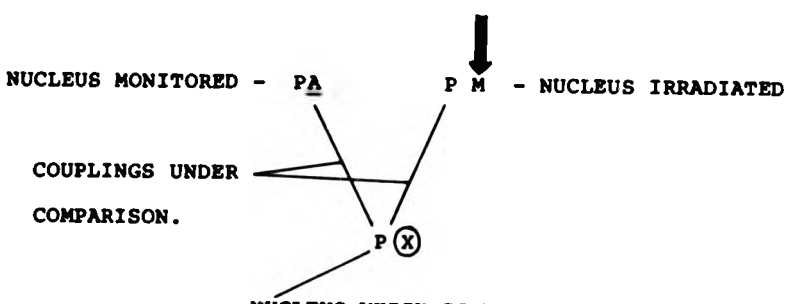


Fig. 2.12. : The diagram shown is used to determine the two coupling constants where relative signs are to be compared.

The relative signs of coupling constants compared are the same if high (low) frequency irradiation is associated with a high (low) frequency perturbation; and opposite when the high (low) frequency irradiation is associated with low (high) frequency perturbation.

In the X part of the spectrum, resonances X3 and X1 in the low frequency region are perturbed; the relative signs of $^{2}J(P_A-P_M)$ and $^{3}J(P_M-P_X)$ are opposite.

EXPERIMENT (iii): Resonance M1 in the low frequency region is irradiated,

(a). the association of P_A and P_M with a particular spin state of P_X may be considered, comparing $^{3}J(P_A-P_X)$ and $^{3}J(P_M-P_X)$.

In the A part of the spectrum, resonances A1 and A2 in the low frequency region are perturbed; the relative signs of these coupling constants are the same, confirming the result obtained in (ia).

(b). The association of P_M and P_X with a particular spin state of P_A may be considered, comparing $^{2}J(P_A-P_M)$ and $^{3}J(P_A-P_X)$.

In the X part of the spectrum, X4 and X2 in the high frequency region is perturbed; the relative signs of $^{2}J(P_A-P_M)$ and $^{3}J(P_A-P_X)$ are opposite.

EXPERIMENT (iv): Resonance X4 in the high frequency region is irradiated,

(a). the association of P_A and P_X with a particular spin state of P_M may be considered, comparing $^{2}J(P_A-P_M)$ and $^{3}J(P_M-P_X)$.

In the A part of the spectrum, resonances A1 and A3 in the low frequency region are perturbed; the relative

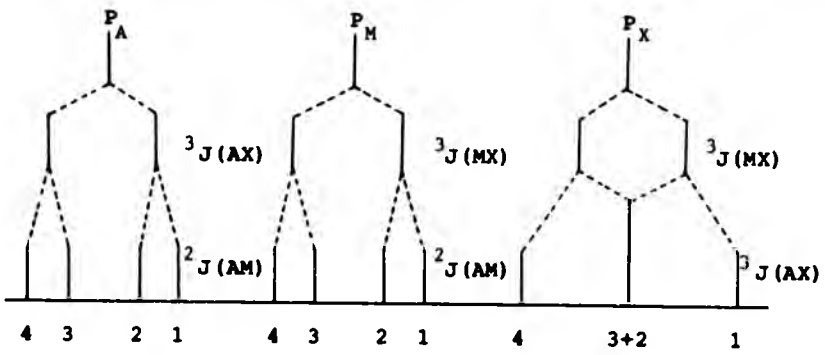


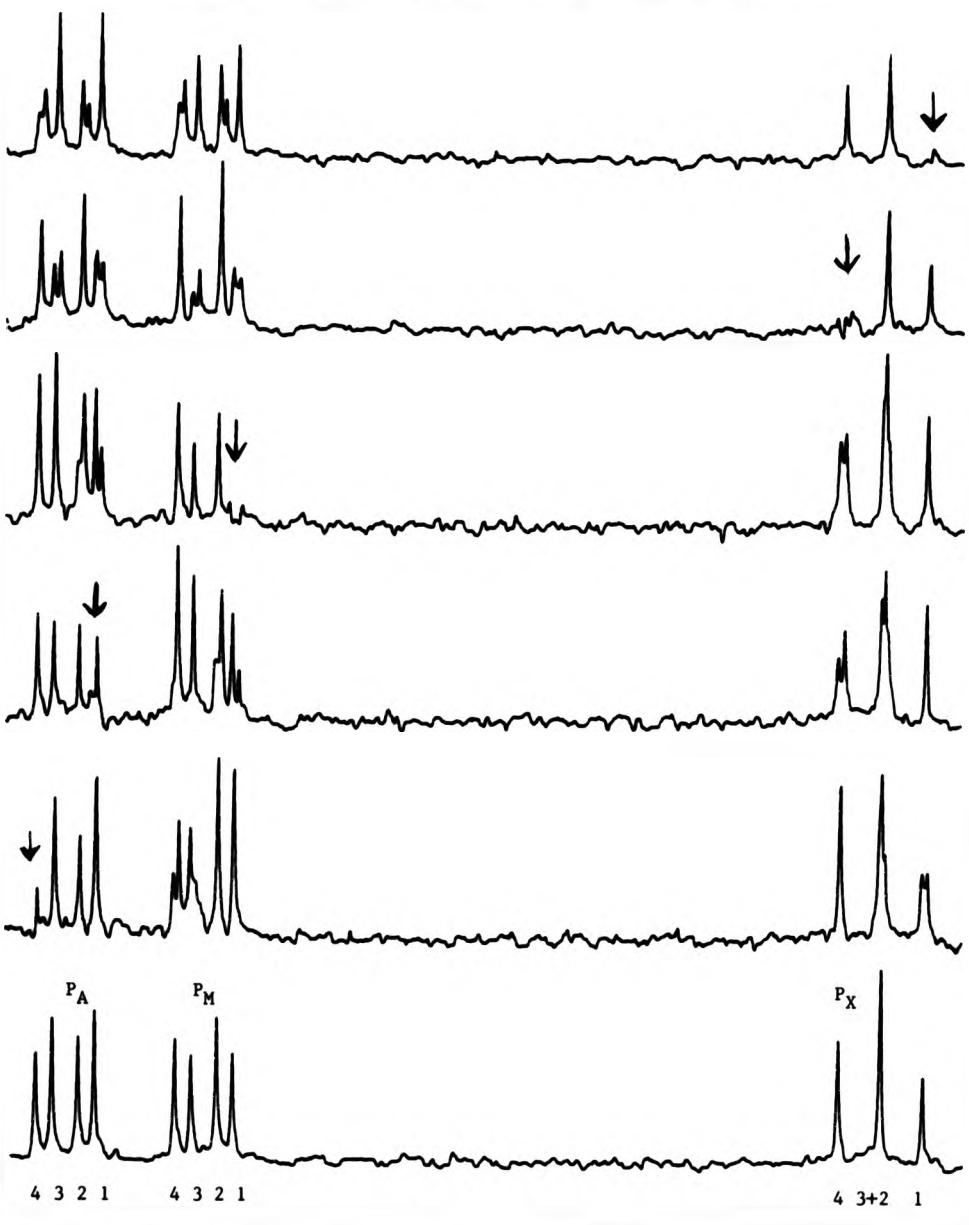
Fig 2.13. : Schematic representation of the ^{31}P n.m.r. spectrum of triphosphine (IX), indicating the numbering scheme used for each resonance.

Table 2.4. : Results from the spin-tickling experiments for triphosphine (IX).

EXPERIMENT	RESONANCE IRRADIATED			RESONANCES PERTURBED		
	P_A	P_M	P_X	P_A	P_M	P_X
(i)	4				4 , 3	1 , 3
(ii)	1				1 , 2	2 , 4
(iii)		1		1 , 2		2 , 4
(iv)			4	1 , 3	1 , 3	
(v)			1	4 , 2	2 , 4	

NOTE All the resonances perturbed are observed as doublets (Spectrum 2.7.)

Spectrum 2.7. : Spin-tickling experiments performed on triphosphine (IX). The arrows show the resonances irradiated and the perturbed resonances are observed as doublet splittings in the ^{31}P n.m.r. spectra. Recorded at 36.2.MHz.



signs of $^{2}J(P_A-P_M)$ and $^{3}J(P_M-P_X)$ are opposite, confirming the result obtained in (ib).

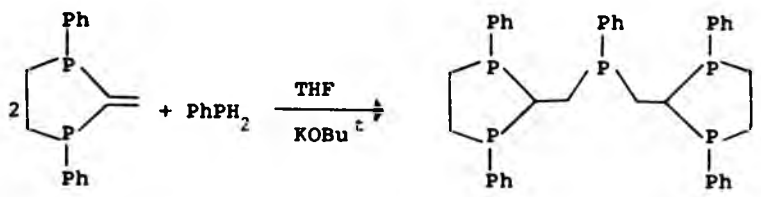
In summary, the results from these experiments reveal that the relative sign of $^{2}J(P-P)$ is negative and $^{3}J(P-P)$ is positive. Thus, for triphosphine (IX), $^{2}J(P_A-P_M) = -12.8Hz$, $^{3}J(P_A-P_X) = +33.6Hz$ and $^{3}J(P_M-P_X) = +33.6Hz$. Additionally, these experiments confirm the assignment of the ^{31}P n.m.r. spectra for triphosphines (VII), (VIII) and (XI).

PENTATERTIARY AND HEXATERTIARY PHOSPHINES.

PREPARATION.

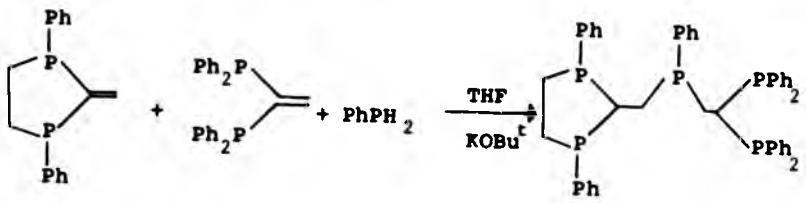
The two new pentatertiary phosphines (XII) and (XIII) have been synthesised by base-catalysis addition, in a manner similar to that employed for the triphosphines (discussed earlier in this chapter). Employing Method 1 (Equation 2.1.), two equivalents of phosphine (Xb) reacted with phenylphosphine at room temperature, resulting in the exclusive formation of phosphine (XII). Attempted analogous preparations of phosphine (XIII) (Equation 2.2.), using 1:1:1 molar ratios of phosphine (Xb), (XIV) and phenylphosphine resulted in the formation of mixtures of related triphosphines (e.g. (VII) and (XV)), in addition to the desired product.

METHOD 1.



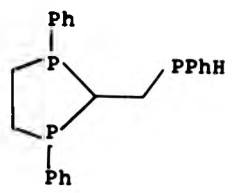
(Xb) (XII)

EQUATION 2.1.



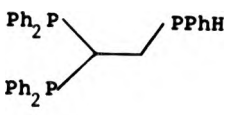
(Xb) (XIV) (XIII)

+



(VII)

+

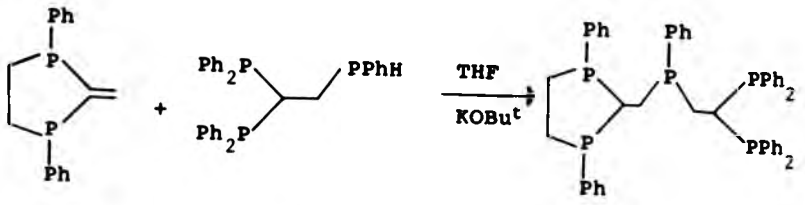


(XV)

EQUATION 2.2.

However Method 2 (Equation 2.3.), using 1:1 molar equivalents of pure triphosphines (XV) and (Xb), resulted in the immediate formation of phosphine (XIII).

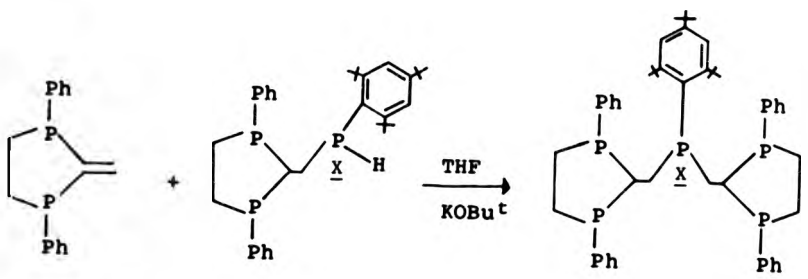
METHOD 2.



(Xb) (XV) (XIII)

EQUATION 2.3.

A further analogous reaction (Fig. 2.14 and Equation 2.4.) was attempted in an effort to prepare the pentatertiary phosphine (XVII) from compounds (Xb) and (VIII).



(Xb) (VIII) (XVII)

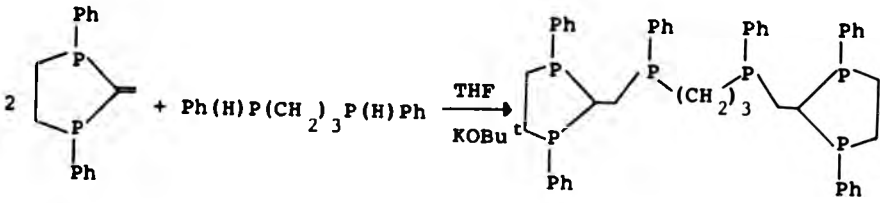
EQUATION 2.4.

Fig. 2.14. : Attempted preparation of the pentatertiary phosphine (XVII).

Unfortunately triphosphine (VIII) underwent no addition reactions, even under reflux. Such additions were probably

prevented by the steric hindrance of the bulky aryl function on the central phosphorus atom X. However, similar addition reactions, where less bulky groups are present on the central phosphorus atom X possessing a hydrogen atom, should lead to the formation of other polytertiary phosphines. Also, variants of Method 2, using other suitable vinylphosphines (e.g. CH_2=CHPPh_4), could yield novel tetratertiary phosphines.

The hexatertiary phosphine (XVI) has been synthesised by base-catalysis addition employing Method 1 (Equation 2.1.) described previously. Two equivalents of phosphine (Xb) reacted with bis-1,3-(monophenylphosphino)propane at room temperature, resulting in the formation of (XVI), Equation 2.5.



(Xb) (XVI)

EQUATION 2.5.

THE ^{31}P N.M.R. SPECTRAL ANALYSIS OF THE PENTATERTIARY PHOSPHINE (XII).

Owing to the *trans* relationship of the two ring phosphorus atoms the pentatertiary phosphine (XII) possesses two chiral carbon atoms and a central pseudochiral phosphorus atom; thus eight stereoisomers are possible (Fig. 2.15).

Pseudo-asymmetry[9] arises when a central atom is linked to two different ligands and to an enantiomeric pair of ligands, i.e. it may be written as $^{31}P(+a)(-a)bc$ *or* as $^{31}P(+a)(+a)bc$ (Fig. 2.16). Such an atom is said to be pseudo-asymmetric when it has the form $^{31}P(+a)(-a)bc$.

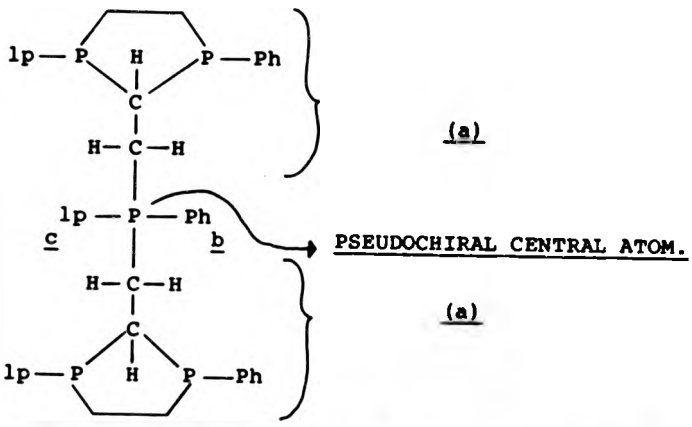


Fig. 2.16.: Demonstration of pseudo-chirality using (XII) as an example.

From the eight possible stereoisomers of ligand (XII) reasons of symmetry predict that:

(1). a≡f, b≡e, c≡h and d≡g are all superimposable

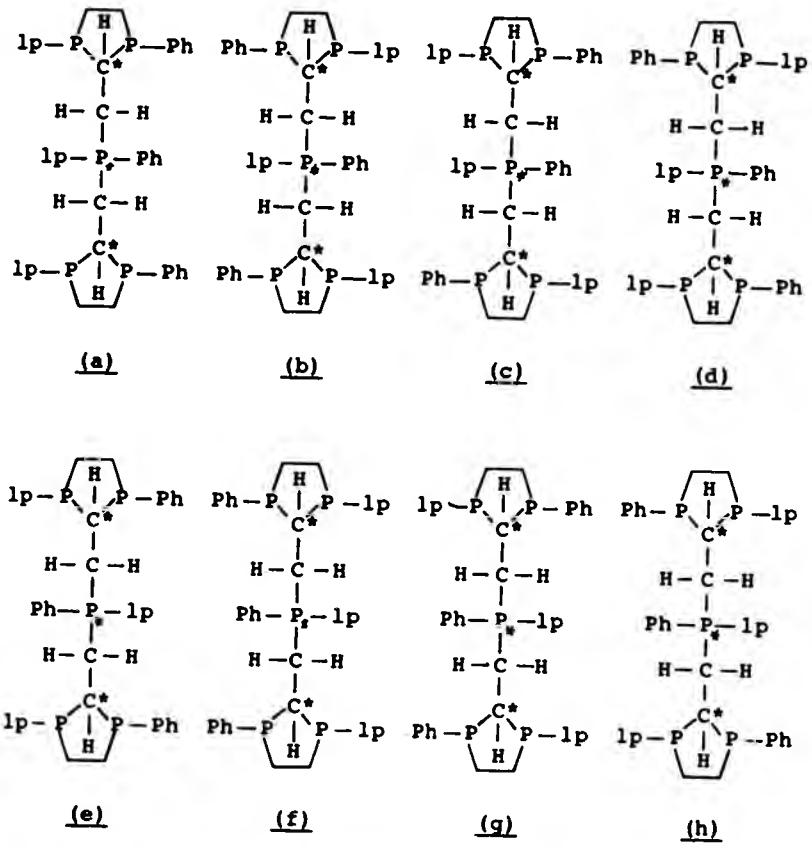


Fig. 2.15.: Diagrams representing the eight possible stereoisomers of ligand (XII). The asterisks indicate the three chiral centres. Each of the ring phosphorus atoms possesses a lone pair of electrons (lp) and a phenyl group but for simplicity only one group is shown for each phosphorus atom, both of which are above or below the plane of the ring with respect to the proton shown attached to the chiral carbon atom; thus reflecting the trans relationship of the ring phosphorus atoms.

enantiomers of each other;

(2). (a/f) and (b/e) are meso pairs because a plane of symmetry is drawn through the central pseudochiral phosphorus atom;

(3). (c/d)and (g/h) are non-superimposable enantiomers of each other when (d) is rotated by 180° from end to end.

Thus, four distinct stereoisomeric forms of ligand (XII) exist, of which three are diastereoisomers:- (a), (b) and (c/d).

N.m.r. studies of enantiomers usually gives rise to identical spectra, thus forms (c) and (d) are indistinguishable by phosphorus n.m.r. spectroscopy. However, applications of chiral solvents and chiral lanthanide shift reagents[10] in the study of enantiomers, often facilitate the induction of different magnetic enviroments in the mirror image modifications, rendering them inequivalent in n.m.r. terms.

The ^{31}P n.m.r. spectrum of (XII) obtained at 24.2MHz is found to show extensive overlapping of the resonances (Spectrum 2.8.), making it impossible to measure unambiguously all the observed splittings. However, the ^{31}P n.m.r. spectrum obtained at 36.2MHz (Spectrum 2.9.), resolved all the resonances and allowed the measurement of the splittings. The large number of resonances necessitated the development of a special method of spectral analysis which is detailed below.

Firstly, the magnitudes of all the splittings were

measured, and then all the related splittings were colour coded. Interestingly, this procedure revealed the existence of three different sets of related splittings, which are taken to arise from three different diastereoisomers (Spectrum 2.9. shows the colour coded resonances.).

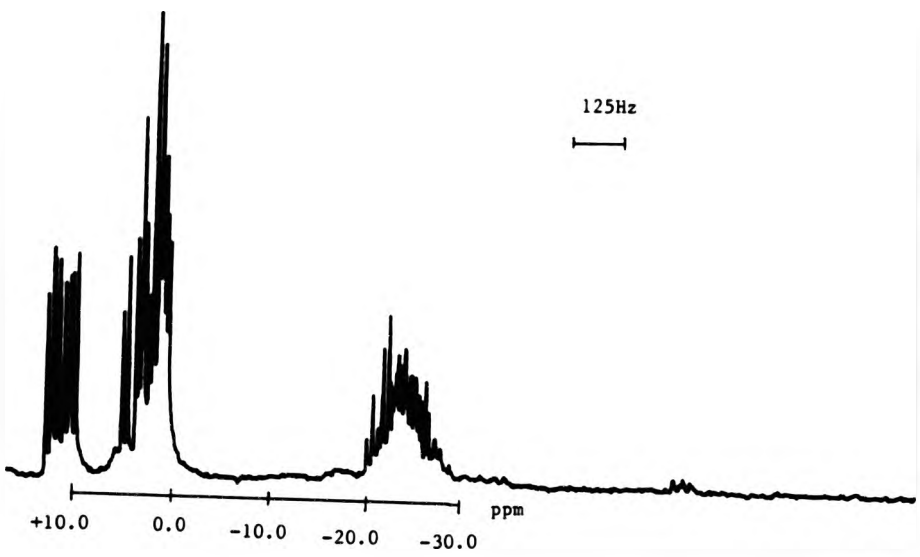
The multiplet structures observed for each of the three sets of colour coded splittings and their related chemical shift positions gave an indication of the type of spin system associated with each diastereoisomer. The green and pink coloured splittings both correspond to a first order AA'BB'X spin system, which relates to the spin systems expected from the configurations of the two diastereoisomers (a) and (b). Arbitrarily, they are respectively given the green and pink colour codes.

The multiplet structures arising from the red and the blue coloured splittings both correspond to first order AMX spin systems, in which the same P_X atom is involved, suggesting that they both originate from one diastereoisomer. Thus, these two sets of splittings are taken to arise from a first order ABMXY spin system which may be that predicted from the configuration of diastereoisomers (c/d). Long range coupling over six bonds can be assumed to be zero so that the AB and XY parts are independent of each other. The ABM subspectrum is colour coded blue, whilst the XYM subspectrum is colour coded red.

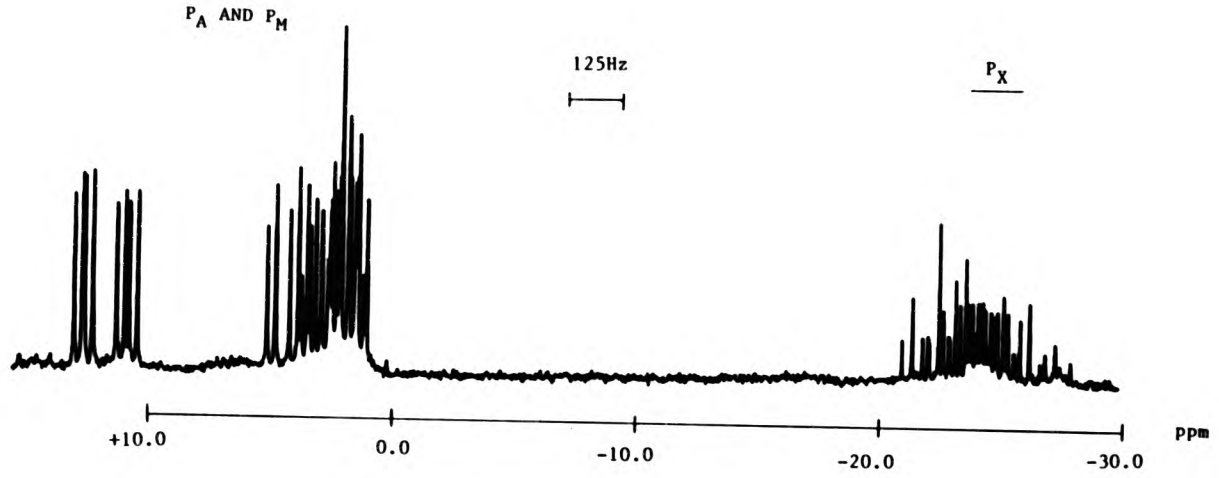
Both these spin systems will be discussed fully later. Overall, the results obtained from the 36.2MHz and 24.2MHz spectra compare favourably.

Diastereoisomers (a) and (b) which give an AA'BB'X

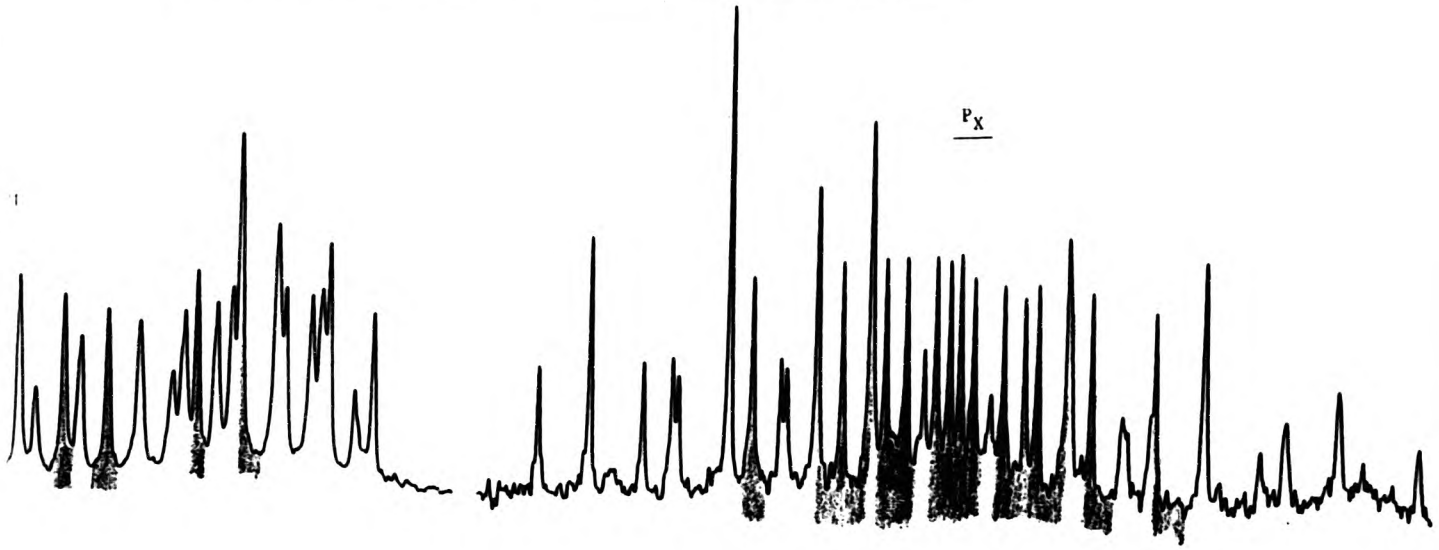
Spectrum 2.8. : ^{31}P n.m.r. spectrum of the pentatertiary phosphine (XII), recorded at 24.2MHz.

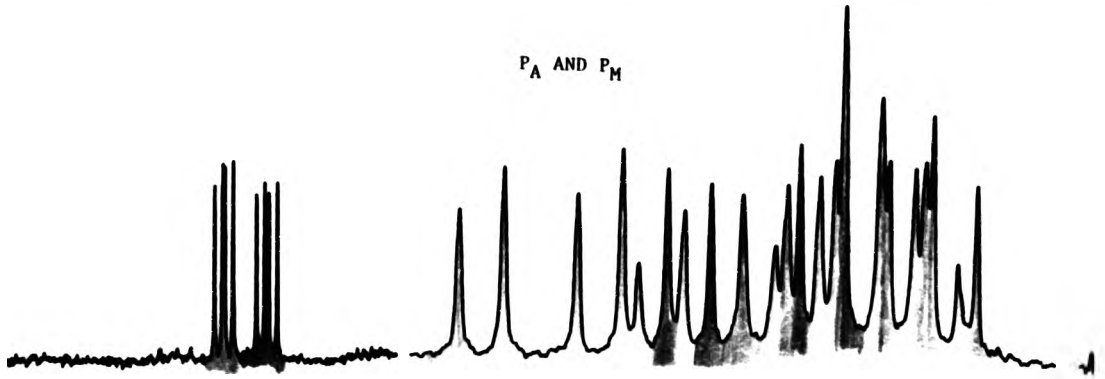


Spectrum 2.9. : ^{31}P n.m.r. spectrum of the pentatertiary phosphine (XII), recorded at 36.2MHz. Original spectrum.

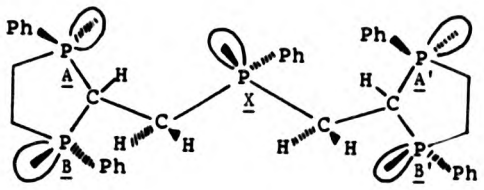


Spectrum 2.9. : ^{31}P n.m.r. spectrum of the pentatertiary phosphine (XII), recorded at 36.2MHz. Expanded spectrum.

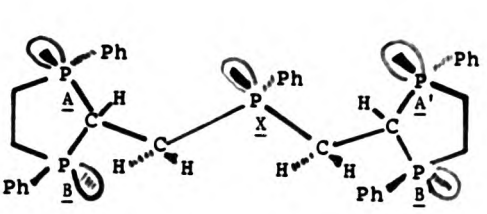




Spectrum 2.9. : ^{31}P n.m.r. phosphine (XII), recorded



(XIIa)



(XIIb)

Fig. 2.17. : The AA'BB'X spin system labelling scheme for diastereoisomers (XIIa) and (XIIb).

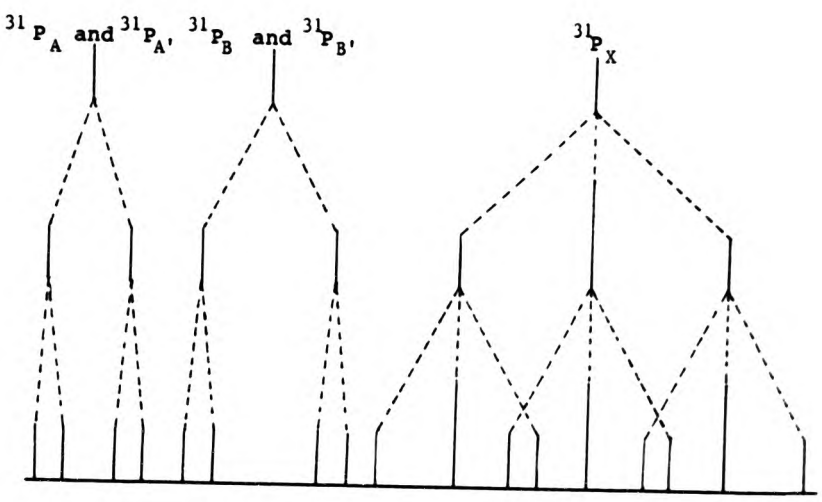


Fig. 2.18. : A schematic representation of a first order AA'BB'X spin system, showing the successive couplings incurred by each phosphorus nuclei.

spin system (Fig. 2.17), in which the six bond couplings $^6J(P_A-P_A)$, $^6J(P_B-P_B)$, $^6J(P_A-P_B)$ and $^6J(P_A-P_B)$ can be taken to be zero and hence this system can be analysed on a first order basis. However, in the P_X part of the spectrum some second order effects are observed. The basic structure of this spin system is depicted in Figure 2.18.

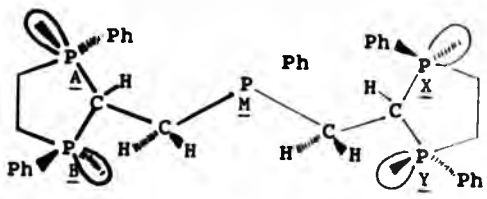
Since P_A and $P_{A'}$ are symmetrically and chemically equivalent nuclei, they would each give rise to four resonances composed of a doublets, indicating two successive couplings, revealing $^2J(P_A-P_B) = {}^2J(P_{A'}-P_B)$ and $^3J(P_A-P_X) = {}^3J(P_{A'}-P_X)$.

Similarly, P_B and $P_{B'}$ undergo the equivalent couplings $^2J(P_A-P_B) = {}^2J(P_{A'}-P_{B'})$ and $^3J(P_B-P_X) = {}^3J(P_{B'}-P_X)$.

In the P_X part of the spectrum, nine resonances are observed consisting of three sets of triplets. These arise from the successive coupling to the P_X nucleus, firstly by the P_B and $P_{B'}$ nuclei and subsequently by the P_A and $P_{A'}$ nuclei.

Diastereoisomers (c/d) are described by a first order ABMXY spin system (Fig. 2.19) and the observed spectrum consists of thirty-two resonances. A first order ABMXY spin system would theoretically consist of eighty resonances, but if the long range couplings over six bonds, such as $J(P_A-P_X)$, $J(P_B-P_X)$, $J(P_A-P_Y)$ and $J(P_B-P_Y)$ are taken to be zero, the spectrum is then simplified to thirty-two resonances, as observed.

As discussed previously, this spectrum reveals the presence of the ABM and XYM spin systems, both of which involve the P_M nucleus. These two spin systems are in fact a first order three spin system, that is the chemical



(XIIc/d)

Fig. 2.19. : Diastereoisomers (XIIc/d) and the ABMXY spin system labelling scheme.

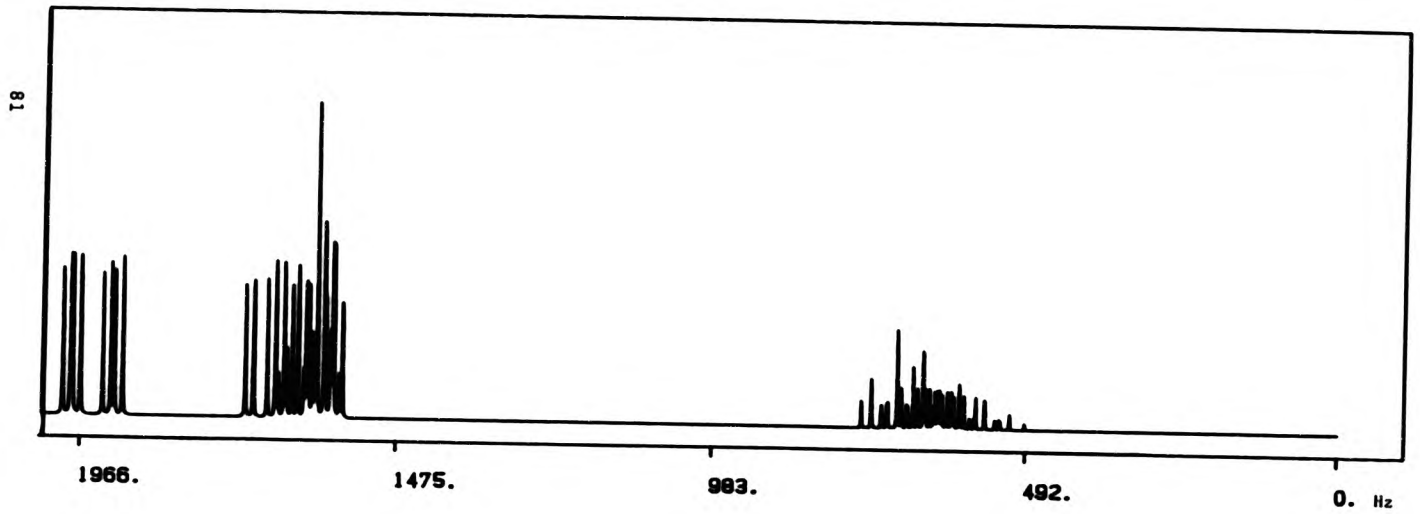
shift differences are $\delta(P_A) - \delta(P_B)$ and $\delta(P_X) - \delta(P_Y)$ which are large.

From the spectrum, the splittings measured for both the ABM and XYM parts of the diastereoisomers are different. A total of sixteen resonances are observed as 'doublets of doublets' in the $P_{A/X}$ and $P_{B/Y}$ region of the Spectrum 2.9. In the P_M part of the spectrum, sixteen resonances are observed consisting of 'doublets of doublets'.

In order to determine whether the splittings observed are in fact coupling constants and then to unequivocally assign the two sets of parameters to each of the three diastereoisomers, a computer simulated ^{31}P n.m.r. spectrum was calculated, using the two sets of approximate parameter values obtained from the 36.2MHz spectrum.

The ^{31}P n.m.r. computer simulated spectrum (Spectrum 2.10.) is found to be consistent with the actual spectrum obtained at 36.2MHz, giving accurate values for the two

Spectrum 2.10. : ^{31}P n.m.r. computer simulated spectrum of the pentatertiary phosphine (XII).



sets of parameters. Table 2.5. contains the measurements of the two parameters obtained from the actual spectrum at 36.2MHz with the accurate values obtained from the calculated spectrum.

The two sets of figures show that the approximate values obtained do not deviate significantly from the accurate values. These results confirm the spectral assignments made for the three diastereoisomers (a), (b) and (c/d) which are formed in an approximate 1:2:4 ratio.

Table 2.5.: ^{31}P n.m.r. data for the pentatertiary phosphine (XII).

DIASTEREOISOMER	CHEMICAL SHIFT, δ, ppm			COUPLING CONSTANT, J, Hz		
	$(P_{A/A'})$	$(P_{B/B'})$	(P_X)	$^2J(P_{A/A'}-P_{B/B'})$	$^3J(P_{A/A'}-P_X)$	$^3J(P_{B/B'}-P_X)$
(XIIa)	+11.8	+1.1	-23.8	(12.2) 12.4	(15.6) 15.6	(40.4) 40.5
(XIIb)	+1.9	+0.4	-27.2	(13.3) 13.3	(39.4) 39.6	(23.3) 22.8

DIASTEREOISOMER	CHEMICAL SHIFT, δ, ppm				
	(P_A)	(P_B)	(P_X)	(P_Y)	(P_M)
(XIIc/d)	+3.4	+0.3	+9.9	+1.6	-25.6

DIASTEREOISOMER	COUPLING CONSTANT, J, Hz					
	$^2J(P_A-P_B)$	$^3J(P_A-P_M)$	$^3J(P_B-P_M)$	$^2J(P_X-P_Y)$	$^3J(P_X-P_M)$	$^3J(P_Y-P_M)$
(XIIc/d)	(12.4) 12.8	(18.5) 18.6	(38.2) 38.2	(13.0) 13.0	(34.3) 34.3	(25.6) 25.6

NOTE

(a) Chemical shifts relative to external 85% H_3PO_4
(b) In THF/C_6D_6 at 25°C.
(c) Values given in the brackets are those obtained from the simulated spectrum.

THE ^{31}P N.M.R. SPECTRAL ANALYSIS OF THE PENTATERTIARY PHOSPHINE (XIII).

Owing to the trans relationship of the ring phosphorus atoms the pentatertiary phosphine (XIII) possesses one chiral carbon atom and a central chiral phosphorus atom, thus a total of four stereoisomers are possible (Fig. 2.20), of which there are only two diastereoisomers [(XIIIa) and (XIIIb)].

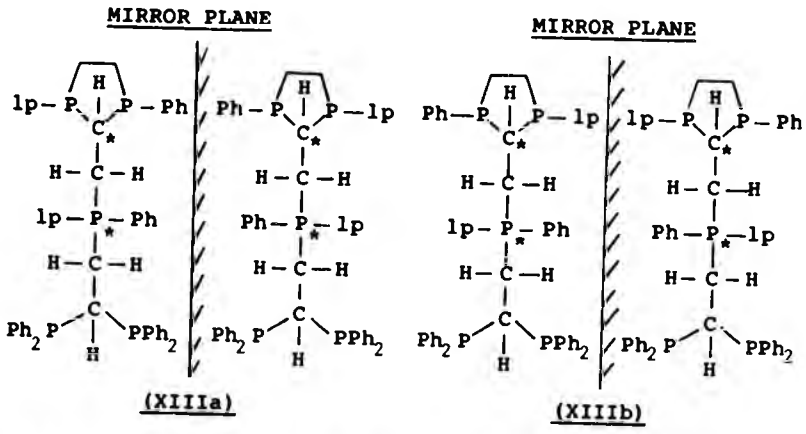


Fig. 2.20. : Diagrams representing the four possible stereoisomers of (XIII) of which (XIIIa) and (XIIIb) are diastereoisomers. The asterisks indicate the two chiral centres. Each of the ring phosphorus atoms possesses a lone pair of electrons (lp) and a phenyl group, but for simplicity only one of the groups are shown for each phosphorus atom, both of which are either above or below the plane of the ring with respect to the proton attached to the chiral carbon atom.

The ^{31}P n.m.r. spectra obtained at 24.2MHz and 36.2MHz, both reveal the presence of the two diastereoisomers (XIIIa) and (XIIIb), which are found to describe a KQXAB spin system. The labelling scheme for spectral analysis is detailed in Figure. 2.21.

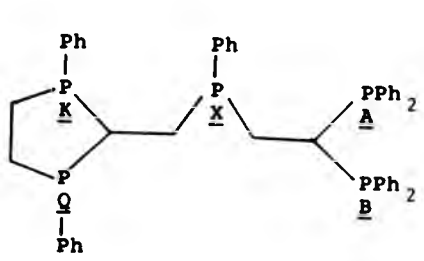


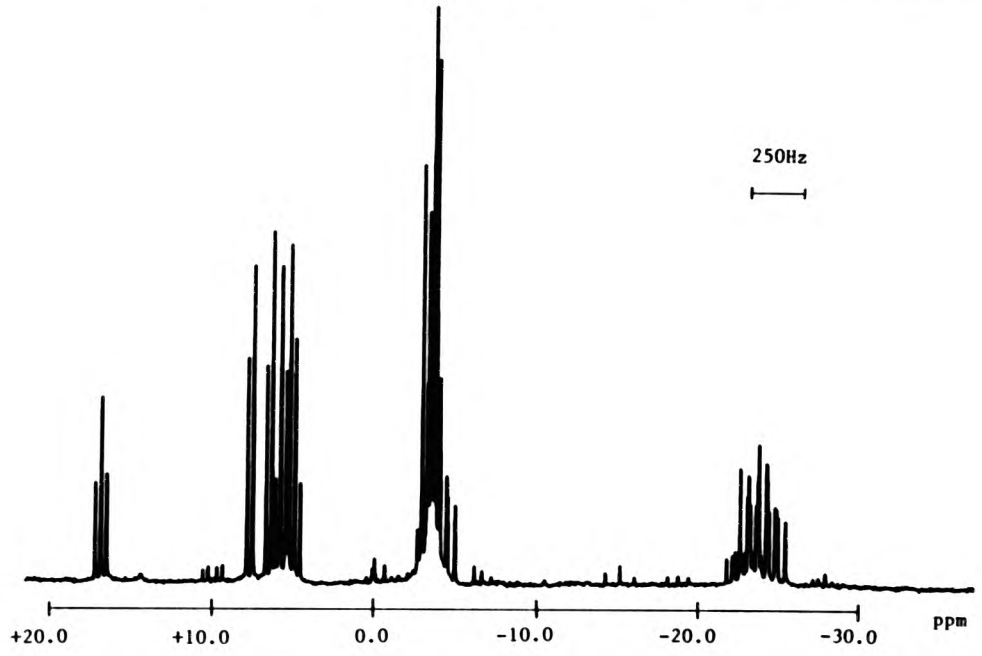
Fig. 2.21. : Labelling scheme for the phosphorus atoms for the pentatertiary phosphine (XIII).

Due to long range coupling over six bonds being zero the KQXAB spin system may be regarded as two separate subsystems.

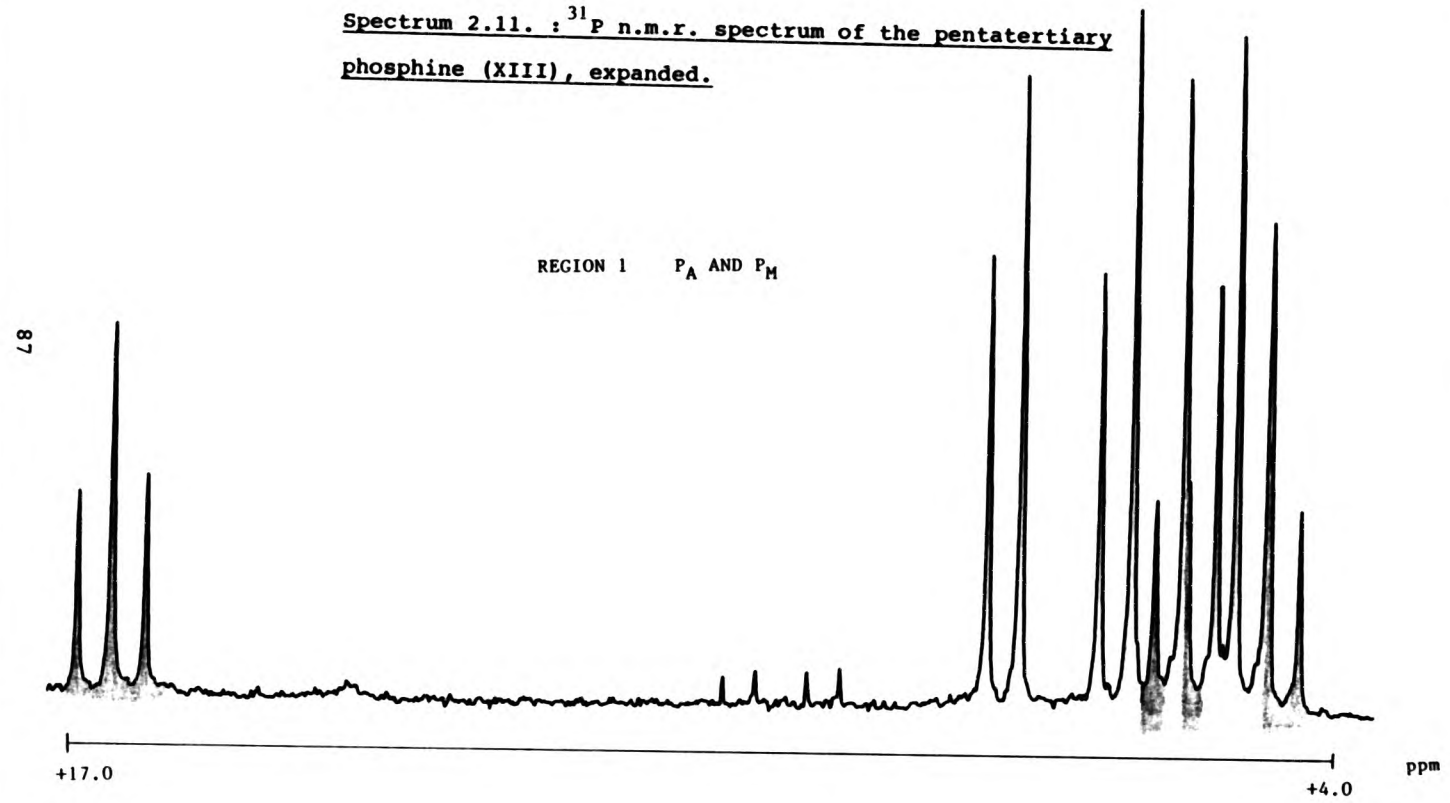
The ^{31}P n.m.r. spectrum obtained at 24.2MHz indicates the presence of four major chemical shift regions with two at high frequency [$\delta(P)$ = +17.3ppm and $\delta(P)$ = +6.9ppm], and two at low frequency [$\delta(P)$ = -3.7ppm and $\delta(P)$ = -23.9ppm] (Spectrum 2.11.).

The resonances at $\delta(P)$ = +17.3ppm appear as a 'simple triplet' with splitting 13.4Hz. The resonances at $\delta(P)$ = +6.9ppm show some overlapping, but some related splittings are measurable of 12.2Hz and 45.2Hz. The

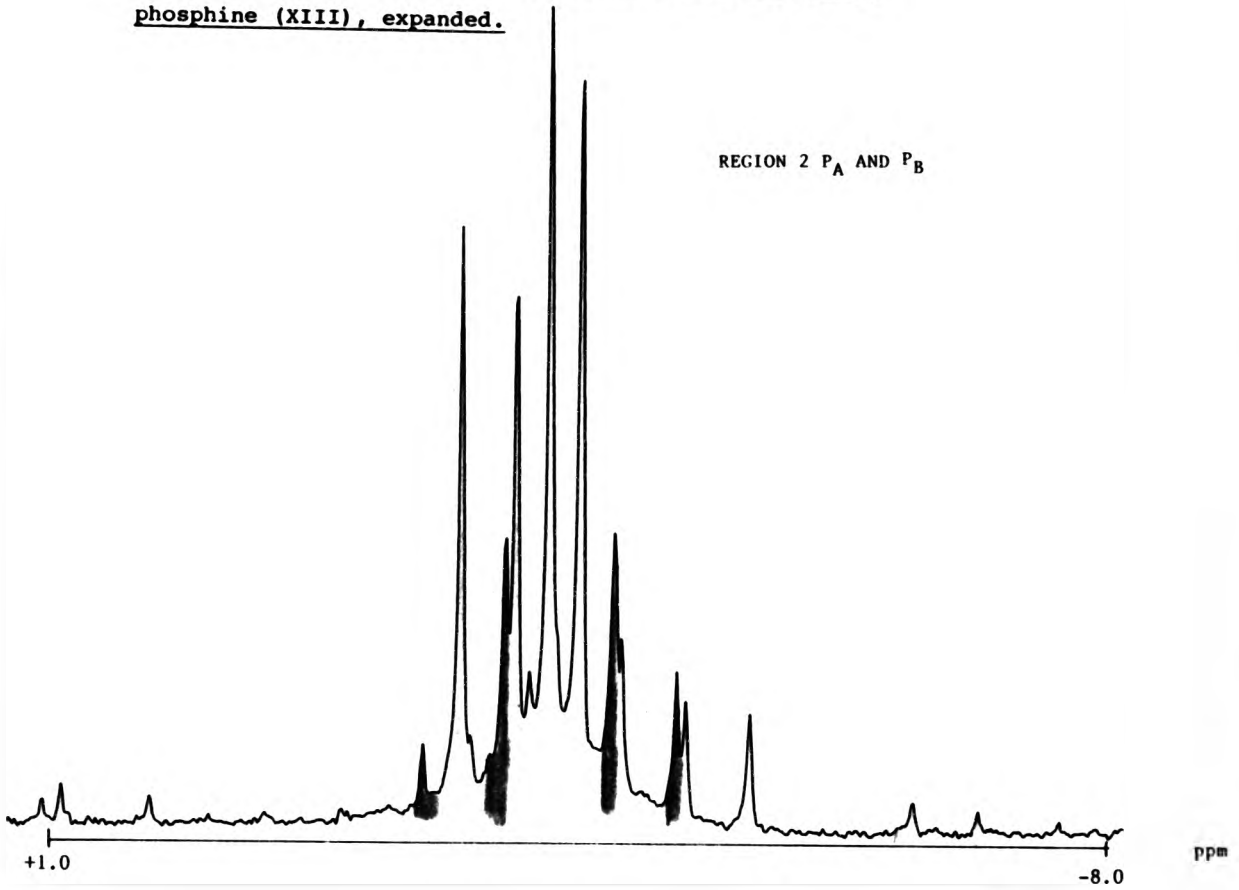
Spectrum 2.11. : ^{31}P n.m.r. spectrum of the pentatertiary phosphine (XIII), recorded at 36.2MHz. Original spectrum.



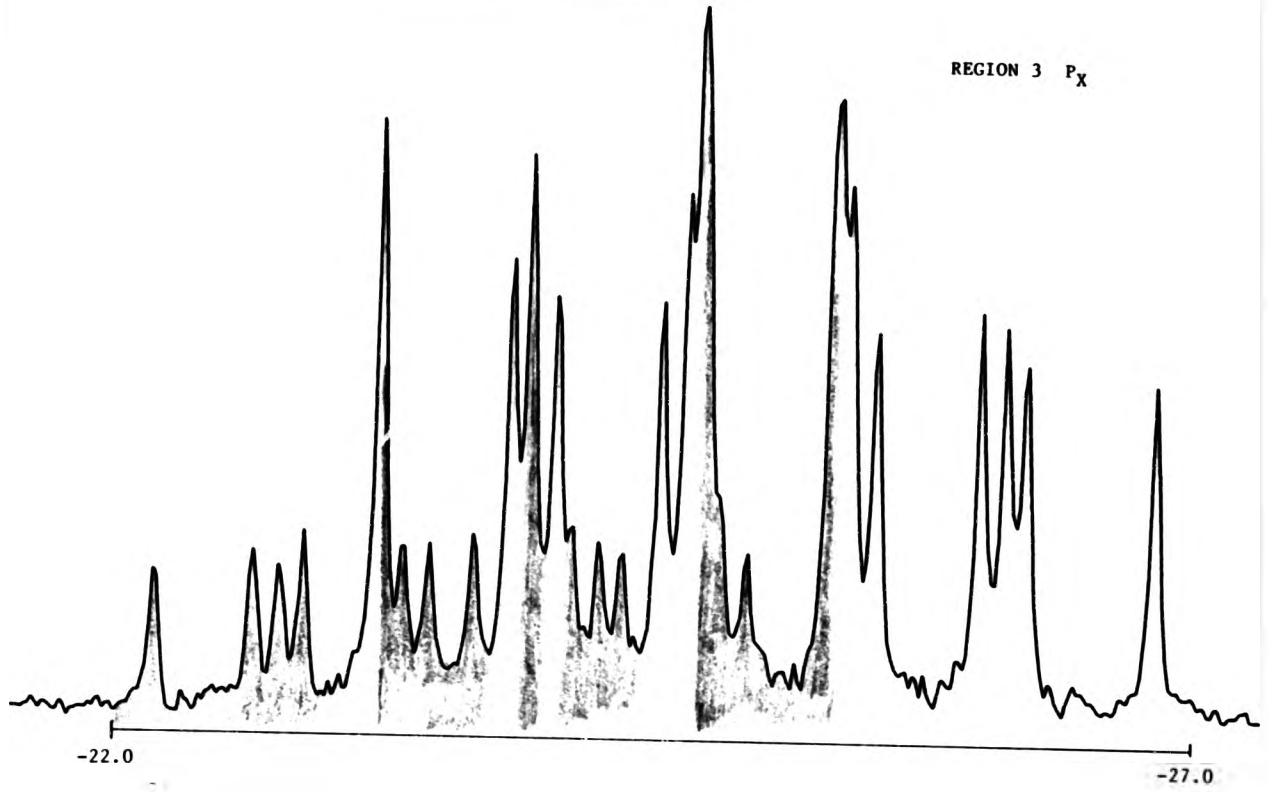
Spectrum 2.11. : ^{31}P n.m.r. spectrum of the pentatertiary phosphine (XIII), expanded.



Spectrum 2.11. : ^{31}P n.m.r. spectrum of the pentertiary phosphine (XIII), expanded.



Spectrum 2.11. :^{31}P n.m.r. spectrum of the pentatertiary phosphine (XIII), expanded.



resonances centred at δ(P) = +4.5ppm, within the δ(P) = +6.9ppm region, show splittings of 12.2Hz and 20.5Hz.

The resonances in the δ(P) = -3.7ppm and δ(P) = -23.9ppm regions show extensive overlapping, which precludes the measurement of any splittings.

The ^{31}P n.m.r. spectrum obtained at 36.2MHz also indicates the presence of four major chemical shift regions at δ(P) = +17.1ppm, δ(P) = +6.1ppm, δ(P) = -3.7ppm and δ(P) = -24.7ppm, which compare favourably with those observed at 24.2MHz. All the resonances can be clearly observed at 36.2MHz; the splittings measured are the same as those measured at 24.2MHz, indicating that they are coupling constants.

The 36.2MHz spectrum shows two sets of resonances with relative intensities in a 4:1 ratio. These sets of resonances are taken to arise from the two diastereoisomers of (XIII) and are referred to as the major and minor diastereoisomers respectively. Thus, there is a method of differentiating between the two diastereoisomers (Spectrum 2.11.).

The resonances observed at δ(P) = +17.1ppm and δ(P) = +6.1ppm arise from a first order AMX spin system. At δ(P) = +17.1ppm, there is a 'simple triplet' with ^{3}J(P-P) = 13.2Hz, but the intensity of the central resonance suggests overlapping. A 'simple triplet' is observed because the magnitudes of the coupling constants ^{2}J(P-P) and ^{3}J(P-P) are very similar.

At δ(P) = +6.1ppm, three distinct groups of 'doublets of doublets' are observed. These may be distinguished by

their various intensities; two arise from the major diastereoisomer and one from the minor diastereoisomer.

The resonances at δ(P) = -3.7ppm arise from the AB part of a second order ABX spin system, and consist of eight resonances with intensity distortions due to second order character. The resonances of the major diastereoisomer can be clearly observed and the following coupling constants were measured: $^{2}J(P_A-P_B)$ = 108Hz, $^{3}J(P_A-P_X)$ = 17.2Hz and $^{3}J(P_B-P_X)$ = 23.9Hz. In the case of the minor diastereoisomer the outer lines of the AB system were too weak to be observed, however the inner lines can be observed.

The resonances at δ(P) = -24.7ppm arise from coupling to the central P_X nucleus, from which values of $^{3}J(P_A-P_X)$ = 17.1ppm and $^{3}J(P_B-P_X)$ = 20.0ppm, can be obtained for the minor diastereoisomer.

The assignment of the two spin systems KQX and ABX to each part of the molecule was possible from previous work conducted on the two phosphines (Xb) and (XIV). From the analysis of ^{31}P n.m.r. spectra of polyphosphorus phosphines synthesised using (Xb) (described previously in this chapter), it is found that they all have a first order AMX spin system with the magnitude of $^{2}J(P_A-P_M)$ in the range of 12.0Hz to 13.0Hz. Thus, the five-membered ring part of $(XIII)_A$ and P_X atom is taken to give rise to the KQX spin system.

The work conducted using phosphine (XIV)[11] has generally led to second order ABX spin systems in which $^{2}J(P_A-P_B)$ is very large (ca>100Hz), since the lone pairs of electrons of the two phosphorus atoms A and B are in a cis orientation. The ABX spin system is therefore assigned to the acyclic

part of (XIII), as the magnitude of $^{2}J(P_{A}-P_{B})$ is large (108Hz), indicating the cis orientation of the lone pairs of electrons of the two phosphorus atoms.

From the notation of the spin systems, it is apparent that for (XIII), the two ring phosphorus nuclei are weakly coupled to each other (KQX), whilst the acyclic phosphorus nuclei are strongly coupled to each other (ABX). This reveals a greater degree of inequivalence of the two ring phosphorus nuclei compared to the acyclic phosphorus nuclei.

It is interesting to note from the analysis of the ^{31}P n.m.r. spectrum of (XIII) the clearly observed lone pairs of electrons 'orientation effect' of the phosphorus atom on the magnitude of $^{2}J(P_{A/K}-P_{B/Q})$ coupling constant.

From the complete analysis of the ^{31}P n.m.r. spectrum, it is found that the values obtained for the coupling constants of both the diastereoisomers are very similar. Fortunately, the significant differences in the relative proportions of the diastereoisomers are reflected in the relative intensities of the resonances arising from each; thus it was possible to assign the two sets of n.m.r. parameters which are presented in Table 2.6., although it is not possible to designate the major and minor diastereoisomers in terms of (XIIIa) and (XIIIb).

Table 2.6.: ^{31}P n.m.r. data for the pentatertiary phosphine (XIII).

DIASTEREOISOMER	CHEMICAL SHIFT, δ, ppm (a),(b)					
	(P_K)	(P_Q)	(P_X)	(P_A)	(P_B)	(P_X)
MAJOR	+7.0	+5.2	-25.2	-2.2	-5.6	-25.2
MINOR	+17.1	+5.0	-24.1	—	—	-24.1

DIASTEREOISOMER	COUPLING CONSTANT, J, Hz.					
	$^2J(P_K-P_Q)$	$^3J(P_K-P_X)$	$^3J(P_Q-P_X)$	$^2J(P_A-P_B)$	$^3J(P_A-P_X)$	$^3J(P_B-P_X)$
MAJOR	12.7	20.5	43.5	108.4	17.6	23.9
MINOR	12.7	13.2	44.0	—	17.1	20.0

NOTE

(a) Chemical shifts relative to external 85% H_3PO_4.

(b) In THF/C_6D_6 at 25°C.

^{31}P N.M.R. SPECTRAL ANALYSIS OF THE HEXATERTIARY PHOSPHINE (XVI).

The trans relationship of the two ring phosphorus atoms results in the hexatertiary phosphine (XVI) possessing two chiral carbon atoms and two chiral phosphorus atoms, thus sixteen stereoisomers are possible and are presented in Figure. 2.22, along with a labelling scheme for the six phosphorus atoms.

The stereochemical inter-relationships between specific stereoisomers of ligand (XVI) are shown in Table 2.7. Due to symmetry reasons, within these sixteen stereoisomers, there are actually six distinct possible diastereoisomers.

The ^{31}P n.m.r. spectrum obtained at 24.2Hz indicates the presence of three major chemical shift regions centred at, δ(P) = +15.5ppm, δ(P) = +7.1ppm and δ(P) = -24.1ppm. Extensive overlapping of the resonances precludes the measurements of the splittings. The ^{31}P n.m.r. spectrum obtained at 36.2MHz is also observed to show three major chemical shift regions centred at, δ(P) = +16.4ppm, δ(P) = +7.9ppm and δ(P) = -23.4ppm (Spectrum 2.12.).

The two exocyclic phosphorus atoms P_X and $P_{X'}$ are separated by four bonds (Fig. 2.22) and the four bond coupling can be taken to be zero; i.e. $^4J(P_X - P_{X'}) \approx 0.0$ppm. It then follows that long range coupling such as $^7J(P_{A/M} - P_X)$, $^7J(P_{A'/M'} - P_X)$, and $^{10}J(P_A - P_{A'})$ are also zero.

Following these assumptions, it is quite reasonable to consider that ligand (XVI) is comprised of two tri-tertiary phosphine subunits, separated from each other at

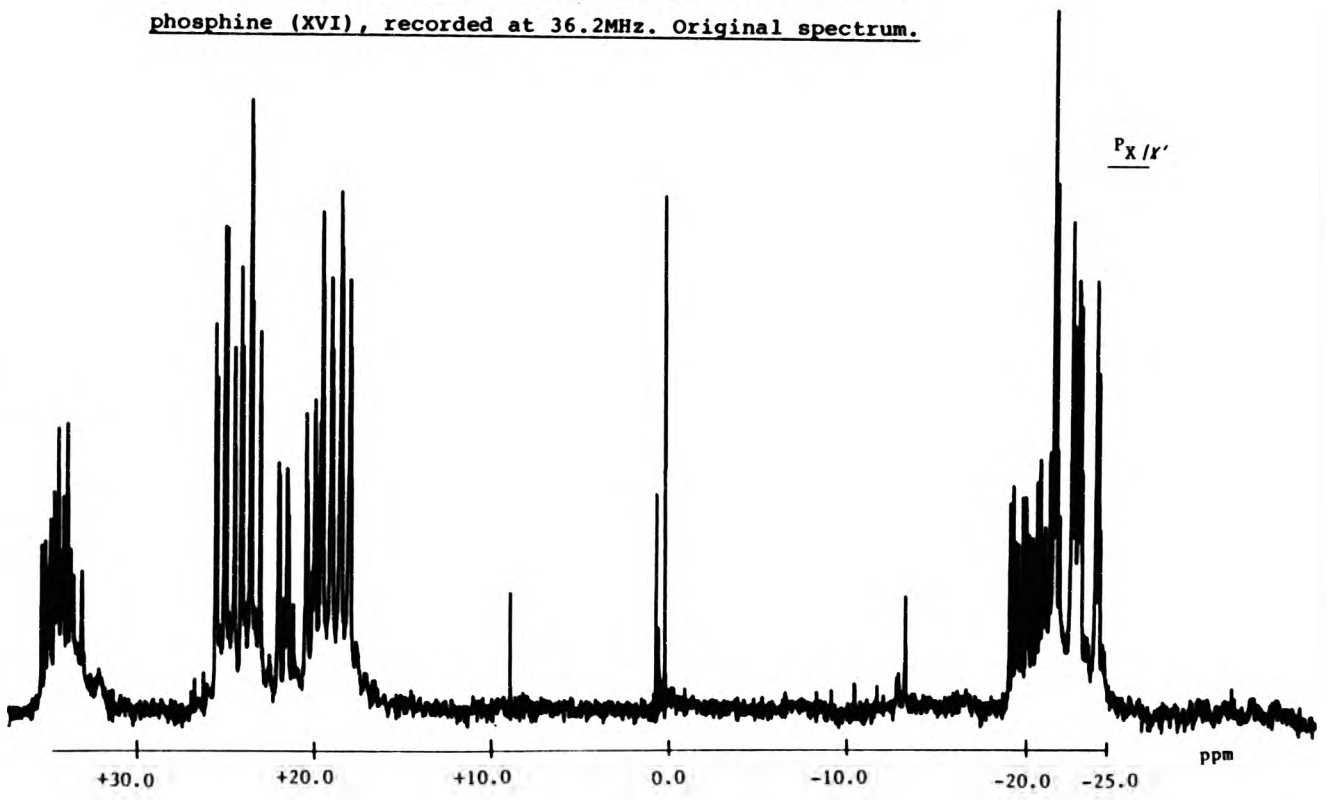
the centre of symmetry as shown in Figure 2.22. Comparison of the two subunits within each of the six diastereoisomers predicts that a total of eight spin systems exist, as shown in Table 2.7.

Consequently, it is feasible to compare these tritertiary phosphine subunits with the tritertiary phosphines (IX) and (XI), previously analysed in this chapter. The ^{31}P n.m.r. spectral analysis of phosphines (IX) and (XI) indicate that they both show first order AMX spin systems, and that the three phosphorus chemical shift positions are found within specfic regions ($\delta(P_A)$ = +9.0ppm to 16.0ppm, $\delta(P_M)$ = +5.5ppm to +17.0ppm and $\delta(P_X)$ = -16.0ppm to -23.0ppm). The three chemical shift regions found for (XVI) are comparable with those noted above for (IX) and (XI). Thus, it may be taken that $\delta(P_{A/A'})$ = +16.4ppm, $\delta(P_{M/M'})$ = +7.9ppm and $\delta(P_{X/X'})$ = -23.4ppm; the data is fully consistent with a first order AMX spin system.

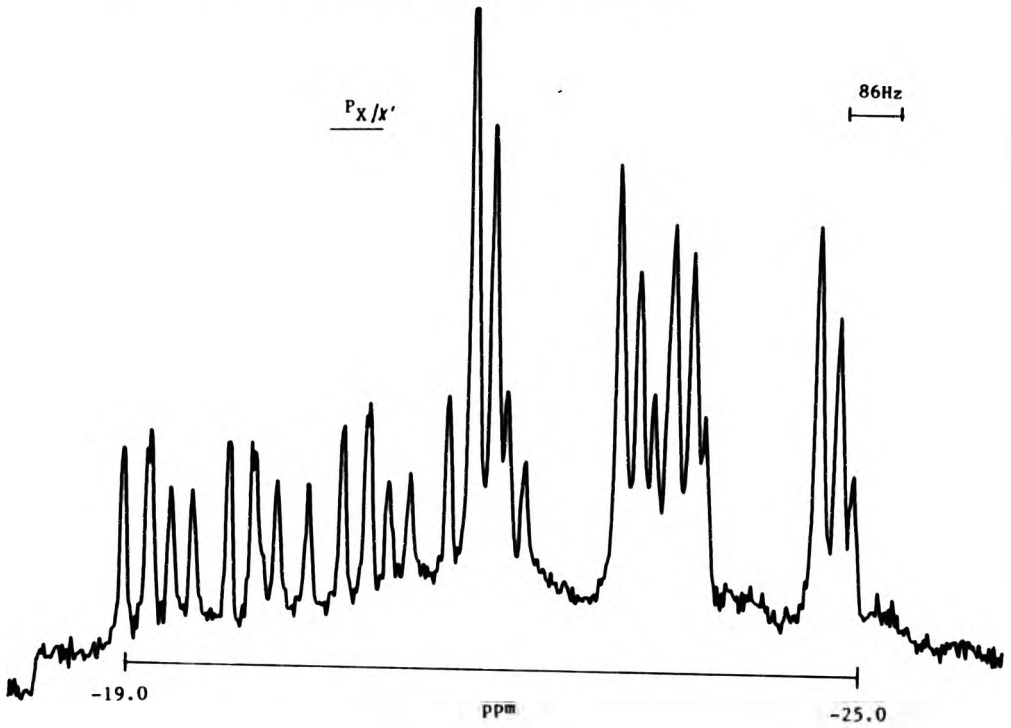
The ^{31}P n.m.r. spectrum obtained at 36.2MHz shows extensive overlapping of the resonances in the $P_{A/A'}$ and $P_{M/M'}$ region, consequently splittings cannot be measured with any accuracy. In the $P_{X/X'}$ region, resonances of two different intensities are observed from which some recurring splittings from 'doublets of doublets' can be measured (Spectrum 2.12.). The high intensity resonances reveal splittings of 26.2Hz and 36.3Hz, and the low intensity resonances, splittings of 4.9Hz and 18.9Hz. It is difficult to proceed further using only the one-dimensional spectrum.

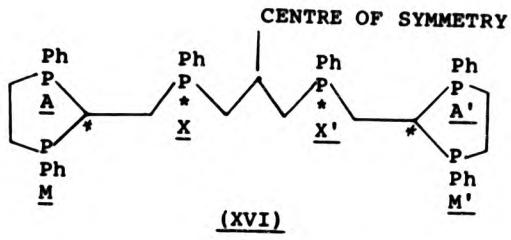
In order to demonstrate the presence of all six

Spectrum 2.12. : ^{31}P n.m.r. spectrum of the hexatertiary phosphine (XVI), recorded at 36.2MHz. Original spectrum.



Spectrum 2.12. : ^{31}P n.m.r. spectrum of hexatertiary phosphine (XVI), showing the $P_{X/X'}$ region expanded.





(XVI)

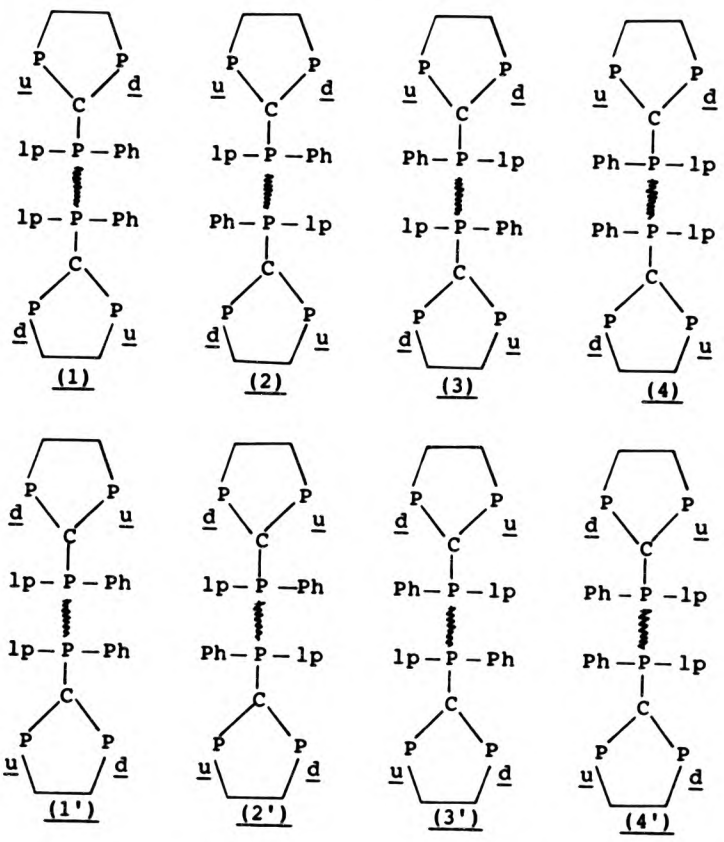
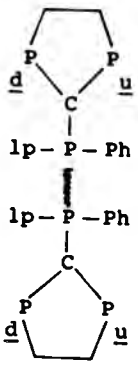
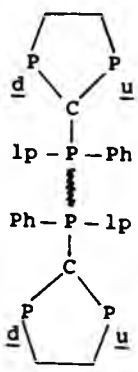


Fig. 2.22 : Diagrams representing the sixteen possible stereoisomers of ligand (XVI). The asterisks indicate the four chiral centres, lp = lone pair of electrons and u = up and d = down represent the Ph(or lp) groups attached to the

phosphorus atoms of the five-membered ring, reflecting the position of each group with respect to the Ph and lp groups attached to the exocyclic $P_{X/X'}$ atom.



(5)



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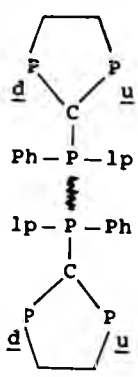

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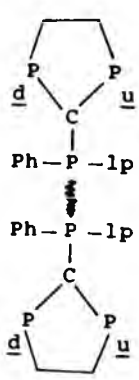

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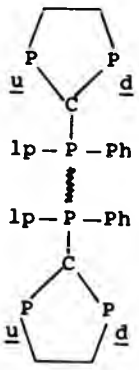

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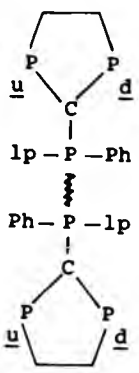

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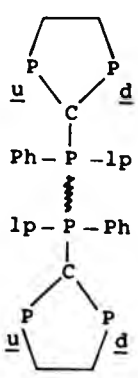

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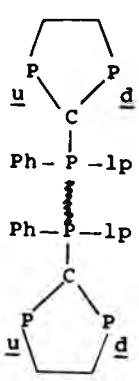
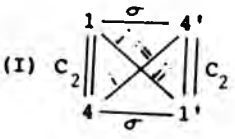
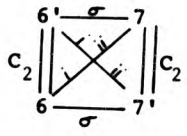
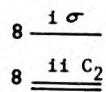
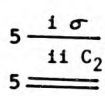


(8')

Table. 2.7. : The stereochemical inter-relationship between specific stereoisomers of the hexatertiary phosphine (XVI).

INTER-RELATIONSHIP BETWEEN THE STEREOISOMERS.	STEREOCHEMISTRY	NUMBER OF SPIN SYSTEMS PREDICTED.
(I) 	1 - 4' 1' - 4 NON-SUPER-IMPOSABLE 1 - 1' ENANTIOMERS. 4 - 4' But, 1 = 4 and 1' = 4' , therefore, only one stereoisomer is possible i.e. 1 - 1' or 4 - 4'.	2
(II) 2 —σ— 3'	NON-SUPERIMPOSABLE ENANTIOMERS.	1
(III) 2' —σ— 3	NON-SUPERIMPOSABLE ENANTIOMERS.	1

INTER-RELATIONSHIP BETWEEN THE STEREOISOMERS.	STEREOCHEMISTRY	NUMBER OF SPIN SYSTEMS PREDICTED.
 (IV)	6 - 7 6' - 7' NON-SUPER-IMPOSABLE 6' - 7 ENANTIOMERS. 6 - 7' But, 6' = 6 and 7' = 7, therefore, only one stereoisomer is possible, i.e. 6 - 7 or 6' - 7'.	2
(V) 	MESO AND SUPER-IMPOSABLE ENANTIOMERS.	1
(VI) 	MESO AND SUPER-IMPOSABLE ENANTIOMERS.	1

Note :

(a) σ - is the reflection in the mirror plane.

(b) C_2 - 180 ° rotation about the plane of the paper at the centre of symmetry.

(c) (i) = First operation = C_2.

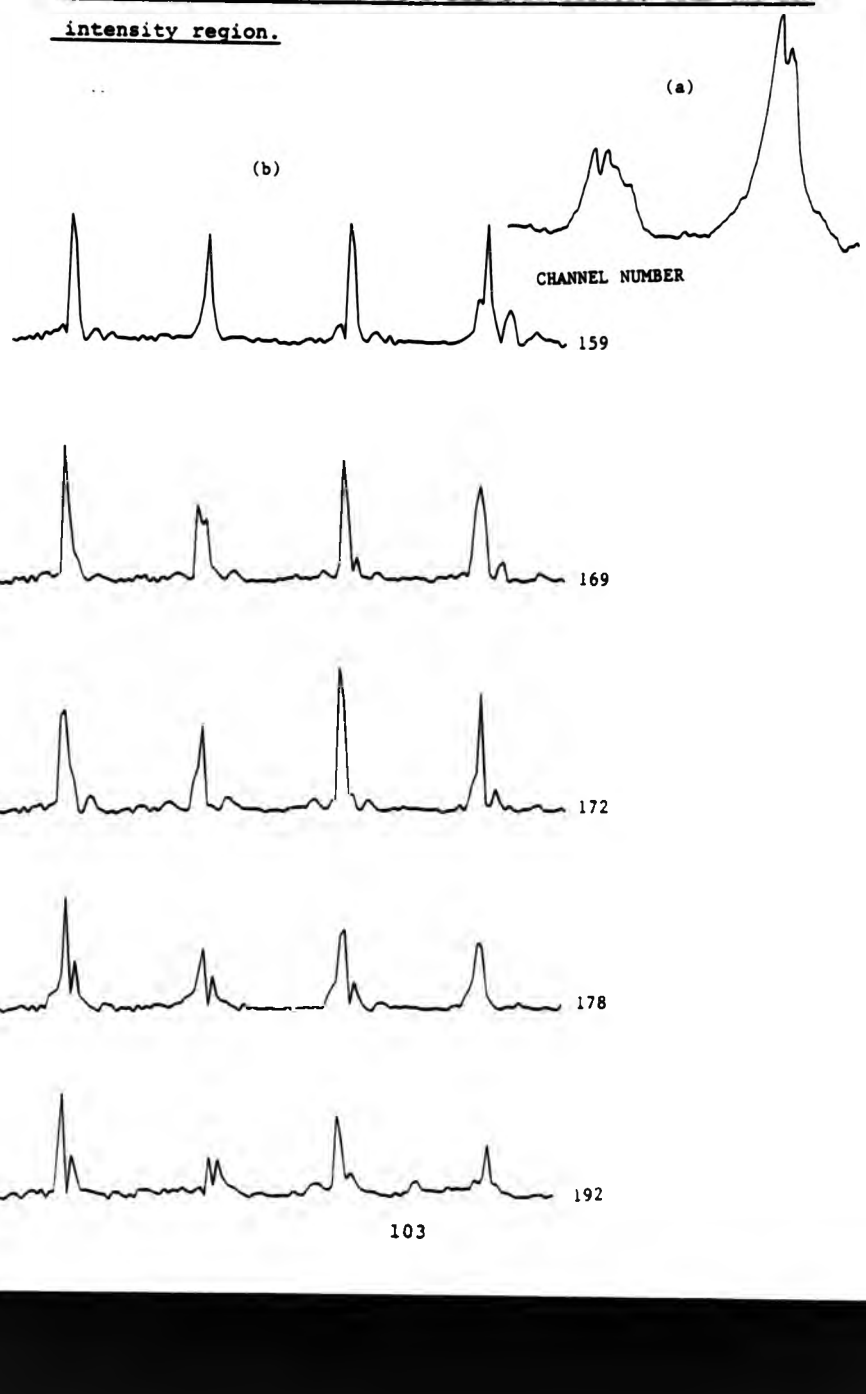
(ii) = Second operation = σ .

diastereoisomers and to obtain some values for chemical shift positions and coupling constants, a two-dimensional J-resolved experiment was undertaken. The $P_{X/X'}$ region was selected for this experiment, as here the resonances were better resolved due to minimal overlap when compared to the $P_{A/A'}$ and $P_{M/M'}$ regions. Additionally, some coupling constants had already been measured for the $P_{X/X'}$ region, again making it most suitable for the two-dimensional study.[12-15]

To simplify the $P_{X/X'}$ region of the spectrum, a 45° two-dimensional homonuclear decoupling experiment was conducted (Spectrum 2.13.). This resulted in the identification of five phosphorus chemical shift positions in the low intensity region and three in the high intensity region. This indicates the presence of eight different $P_{X/X'}$ nuclei arising from the eight different spin systems, predicted for the six diastereoisomers (Table 2.7.). Each of the eight chemical shift positions were then used to obtain the 45° two-dimensional J-resolved slices, from which the coupling constants $^3J(P_{A/A'}-P_{X/X'})$ and $^3J(P_{M/M'}-P_{X/X'})$ were derived (Spectra 2.13b. and 2.14.).

All the two-dimensional J-resolved slices are observed as 'doublets of doublets'; the splittings are essentially first order and are assigned to the different $^3J(P\text{-}P)$ coupling constants. The results are presented in Table 2.8. The total one-dimensional spectrum compares favourably with the decoupled spectrum to indicate that the two sets of different relative intensities observed in the $P_{X/X'}$ region are real.

Spectrum 2.13. : (a) A 45° two-dimensional homonuclear decoupled spectrum of the $P_{X/X'}$ region. The result reveals eight different phosphorus signals.
(b) Five 45° two-dimensional J-resolved slices, from the low intensity region.



Spectrum 2.14. : Three 45° two-dimensional J-resolved slices, from the high intensity region.

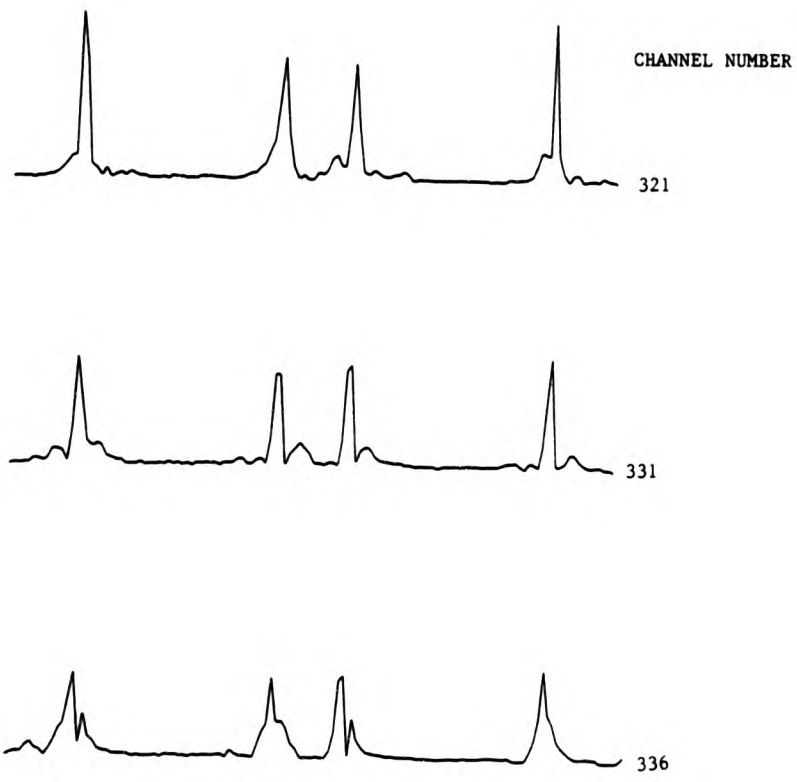


Table 2.8. : Splittings obtained from the 45 ° 2-dimensional J-resolved slices of (XVI).

DATA OBTAINED FROM THE HIGH INTENSITY RESONANCES		
SLICE (CHANNEL NUMBER)	$\delta(^{31}P_{X/X'})$, ppm	SPLITTINGS, Hz
321	-24.1	36.3 and 25.3
331	-24.2	36.3 and 25.3
336	-24.3	36.3 and 25.3

DATA OBTAINED FROM THE LOW INTENSITY RESONANCES		
SLICE (CHANNEL NUMBER)	$\delta(^{31}P_{X/X'})$, ppm	SPLITTINGS, Hz
192	-22.8	39.4 and 21.3
178	-22.6	39.4 and 20.0
172	-22.6	39.4 and 18.8
169	-22.5	39.4 and 19.4
159	-22.3	39.4 and 18.8

It is not possible to fully analyse the total one-dimensional spectrum because of the large number of overlapping resonances. Thus, even though values for $^{3}J(P\text{-}P)$ coupling constants have been obtained (Table 2.8.), it is not possible to specifically assign to each of the six diastereoisomers.

A total analysis of the ^{31}P n.m.r. spectrum and subsequent assignment for the six diastereoisomers may possibly be achieved using a higher field spectrometer, providing enhanced resolution of the overlapping regions.

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CHAPTER 3.

SULPHUR DERIVATIVES OF THE CYCLIC ORGANOPHOSPHORUS COMPOUND (Xb) AND THE RELATED POLYORGANOPHOSPHORUS COMPOUNDS (IX), (XII) AND (XIII).

INTRODUCTION

The process of sulphurisation can provide a useful model for the types of complexes that might be formed by the reactions of cyclic organophosphines and a range of metal substrates. A few preliminary attempts were made to study the novel cyclic triphosphines with metal carbonyls, but significant decomposition of the cyclic triphosphines occurred under the conditions used. Therefore, the new cyclic tertiary diphosphine (Xb) and the related tri- ((IX)) and penta-tertiary ((XII) and (XIII)) phosphines have been sulphurised to provide a guide to its potential coordination chemistry.

The chemical shifts of sulphurised tertiary phosphines has been found to lead to a high frequency increase of ca 50ppm,[1-4] reflecting the change in phosphorus oxidation state. It will be demonstrated later that sulphurisation of the cyclic phosphines occurs with retention of configuration at the phosphorus atom. Thus, as the two ring phosphorus atoms have lone pairs of electrons that are trans orientated, it is to be expected that the P=S groups will also be trans. Since it is possible to systematically sulphurise each of the phosphorus atoms in phosphines (Xb),

(IX), (XII) and (XIII) by the method used for sulphurisation (discussed below), their changes in oxidation state (i.e. the changes in hybridisation), may be investigated by phosphorus n.m.r. spectroscopy.

The change in oxidation state of the phosphorus atom and its effect on the magnitude of the $^{n}J(P-P)$ coupling constants (n = 2 or 3) is discussed in some detail with respect to cyclic triphosphine (IX). As discussed in Chapter 1, a number of factors have to be taken into account when considering the magnitude of $^{n}J(P^{III}-P^{III})$, similarly various factors need to be considered to explain the changes observed for the magnitude of $^{2}J(P^{III}-P^{V})$ and $^{3}J(P^{III}-P^{V})$ due to the effect of sulphurisation and the presence of the five-membered ring system;

(1) The change in hybridisation of the phosphorus atom upon sulphurisation. The change in hybridisation from close to p^3 character in phosphorus (III) compounds where the non-bonding 3s pair of electrons play only a minor role in the bonding pathway, to approaching sp^3 hybridisation in phosphorus (V) compounds results in the s-character of the bonding orbitals used by the phosphorus atom increasing and correspondingly enhancing $^{n}J(P^{V}-P^{V})$.[1,5]

(2) Reaction mechanism. Since sulphurisation occurs with retention of configuration[6-8] at the phosphorus atom, it would be reasonable to assume that the conformation of the ring phosphorus atoms would not be affected greatly on sulphurisation. Additionally, the magnitudes of $J(P^{V}-P^{V})$ couplings are not usually affected to any great extent by conformational changes.[9] However, from the analysis of the

sulphurised species of cyclic triphosphine (IX) the great variations in the values of $^{2}J(P^{III}\text{-}P^{V})$ and $^{3}J(P^{III}\text{-}P^{V})$ can be explained in terms of conformational changes of the five-membered ring.

As discussed in Chapter 1, similar to the metal-chelated ligands forming five-membered rings, the $^{2}J(P\text{-}P)$ coupling constant for the five-membered ring system would be an algebraic combination of both $^{2}J(P\text{-}^{13}C\text{-}P)$ and $^{3}J(P\text{-}^{13}C\text{-}^{13}C\text{-}P)$.[10]

Experimentally, sulphurisation of (Xb), (IX), (XII) and (XIII) was straightforward: half equivalents of elemental sulphur were added to a benzene solution of the cyclic phosphine at room temperature. ^{31}P n.m.r. spectra were obtained after each addition of elemental sulphur until full sulphurisation of the phosphine was obtained. The fully sulphurised species of cyclic phosphines (Xb) and (IX) were isolated as white crystals (see Experimental Chapter 5).

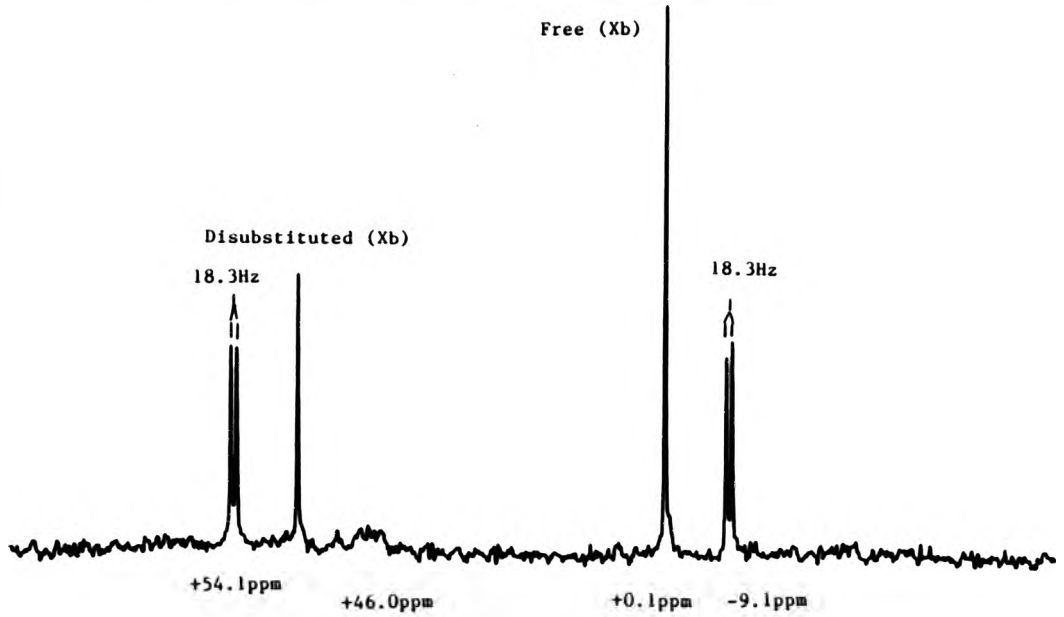
^{31}P N.M.R. SPECTRAL ANALYSIS OF THE SULPHURISATION OF CYCLIC DIPHOSPHINE (Xb).

Cyclic diphosphine (Xb) is the trans isomer of (X) which has been described in Chapter 2 Section A. The ^{31}P n.m.r. spectrum obtained from a solution containing half an equivalent of elemental sulphur and one equivalent of (Xb), (δ(P) = -0.9ppm) shows a first order AX spin system, at δ(P) = -9.1ppm and δ(P) = +54.1ppm, with $^{2}J(P_A-P_X)$ = 18.3Hz (Spectrum 3.1.). The doublet at δ(P) = -9.1ppm arises from the unsulphurised phosphorus (III) atom, whilst the doublet at δ(P) = +54.1ppm arises from the sulphurised phosphorus (V) atom (Fig. 3.1).

Fig. 3.1 : Diagrammatic representation of the two mono-sulphurised species of (Xb).

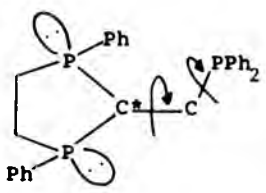
The fully sulphurised species is observed as a singlet at δ(P) = +46.0ppm.

Spectrum 3.1. : ^{31}P n.m.r. spectrum of the sulphurised cyclic diphosphine (Xb), recorded at 36.2MHz.



^{31}P N.M.R. SPECTRAL ANALYSIS OF THE SULPHURISATION OF TRIPHOSPHINE (IX).

The ^{31}P n.m.r. spectral analysis of triphosphine (IX) (Chapter 2.) shows the presence of one first order AMX spin system, revealing the presence of only one diastereoisomer. The lone pairs of electrons of the two ring phosphorus atoms have been found to be <u>trans</u> to each other. Although the carbon atom C* is chiral, free rotation about the carbon-phosphorus bonds as well as the presence of the two phenyl groups on the exocyclic phosphorus atom result in the existence of only one configuration of (IX). (Fig. 3.2, further details in Chapter 2.)



<u>Fig. 3.2. : Diagrammatic representation of triphosphine (IX), showing the free rotation about the carbon*-carbon and carbon-phosphorus bonds.</u>

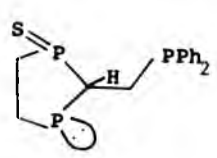
Seven possible sulphurised derivatives of (IX) can be formulated on the assumption that no inversion of configuration at the phosphorus atom occurs, as shown in Figure 3.3. They are:-

(i). Three types of monosulphurised species (a-c);

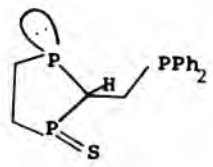
(ii). Three disulphurised species (d-f); and

(iii). One fully sulphurised species (g).

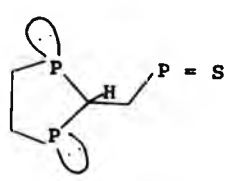
(i) : MONOSULPHURISED SPECIES OF (IX).



(a)

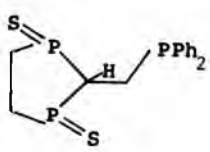


(b)

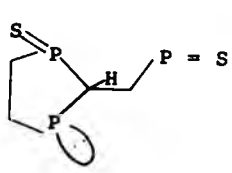


(c)

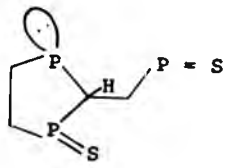
(ii) : DISULPHURISED SPECIES OF (IX).



(d)

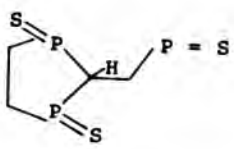


(e)



(f)

(iii) : TRISULPHURISED SPECIES OF (IX).



(g)

Fig. 3.3. : Diagrammatic representation of the seven possible sulphur substituted species of (IX).

The ^{31}P n.m.r. spectrum obtained at 36.2MHz of a solution containing a ratio of two equivalents of sulphur to one equivalent of (IX) in benzene, indicates the presence of eight different spin systems (Spectrum 3.2.).

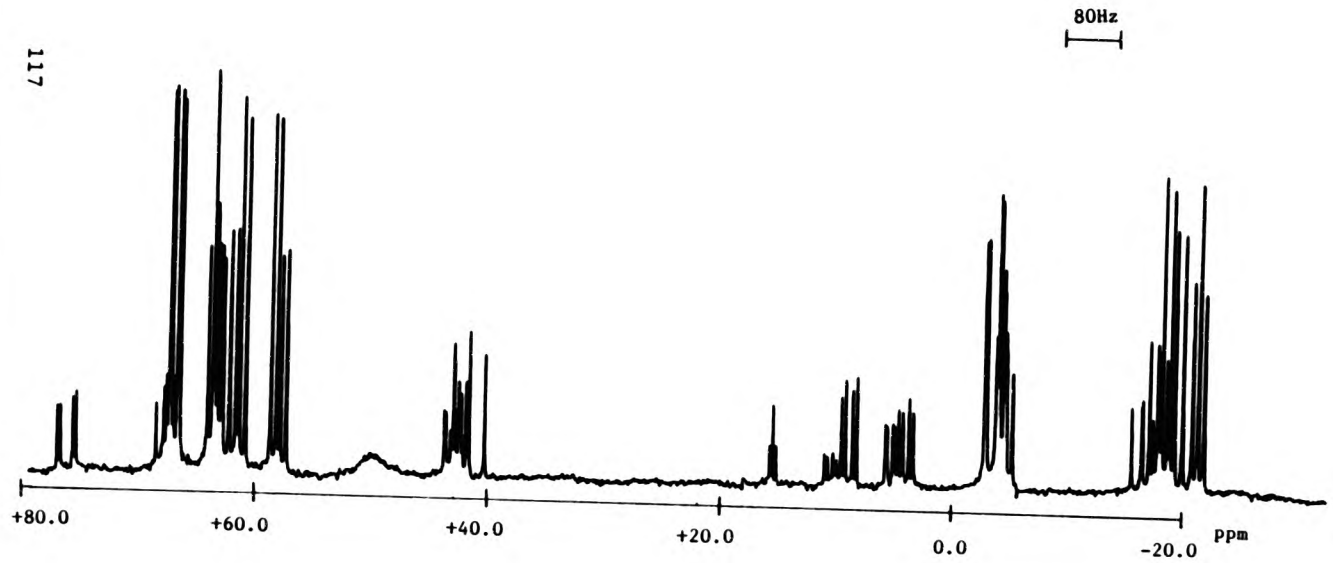
One of these spin systems may be identified as originating from unsulphurised (IX) (first order AMX spin system, shown by the yellow coloured resonances in Spectrum 3.2.). Here, the n.m.r. parameters are $\delta(P_A)$ = +8.7ppm, $\delta(P_M)$ = +3.8ppm and $\delta(P_X)$ = -16.5ppm, and the coupling constants are $^2J(P_A\text{-}P_M)$ = 12.8Hz, $^3J(P_A\text{-}P_X)$ = 33.6Hz and $^3J(P_M\text{-}P_X)$ = 33.6Hz and compare favourably with those known for an authentic sample of (IX)

On examination of the total spectrum, four major chemical shift regions were identified and some general assignments were made. Using these together with a detailed study of the splitting patterns, it was possible to completely assign the spectrum.

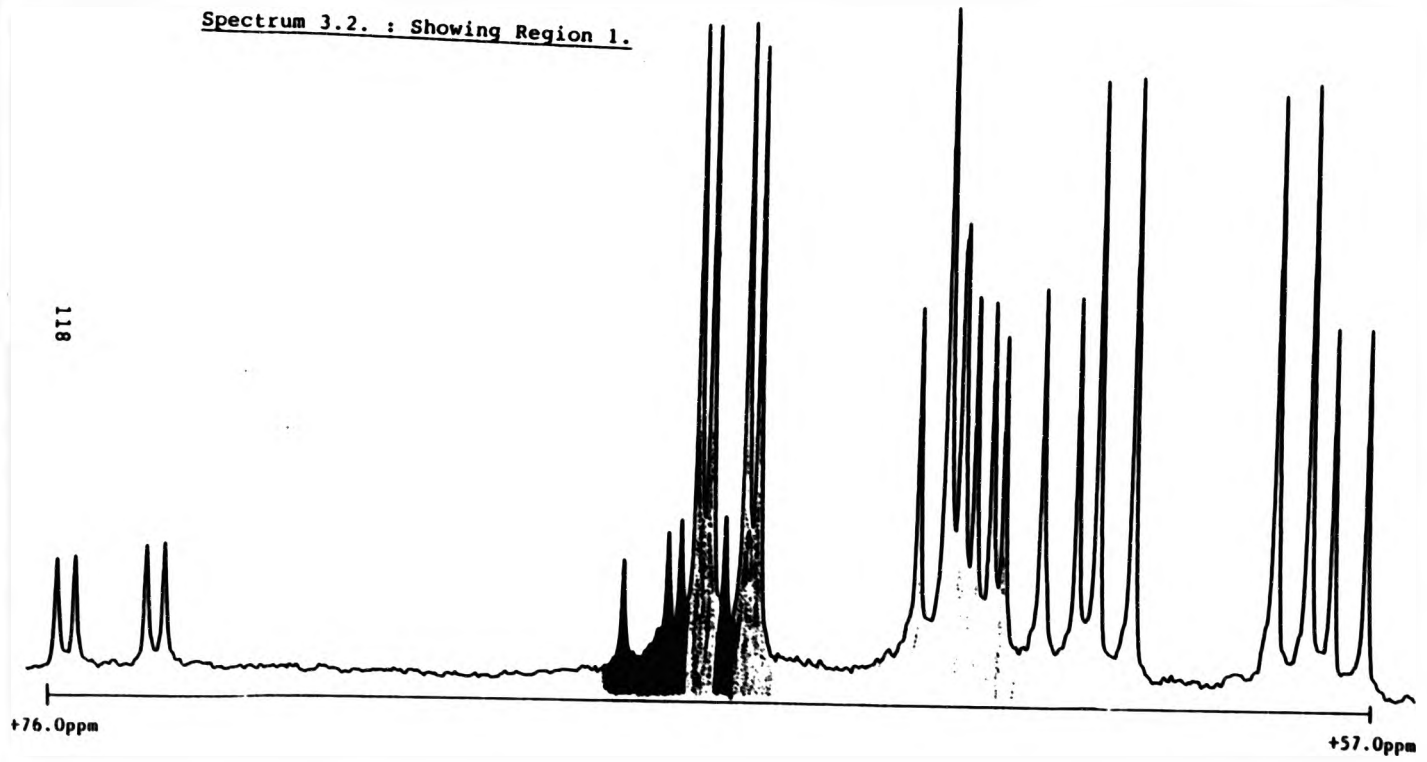
(1) REGION 4.

The group of resonances in the low frequency spectral region between δ(P) = -16.0ppm and δ(P) = -22.0ppm are in the same region as those for the exocyclic P_X atom of (IX). As this is also in the phosphorus (III) resonance area it is reasonable to presume that they arise from unsulphurised exocyclic phosphorus atoms; in species in which none, one or both of the associated ring phosphorus atoms may be sulphurised. Thus these resonances arise from species (a), (b) and (d) in Figure 3.3 (and of course the parent (IX); the relevant phosphorus atoms are indicated in Figure 3.4.

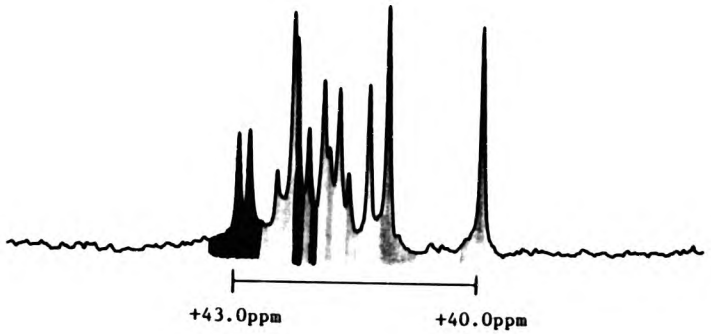
Spectrum 3.2. : ^{31}P n.m.r. spectrum of sulphurised triphosphine (IX) containing two equivalents of sulphur, recorded at 36.2MHz. Original spectrum.



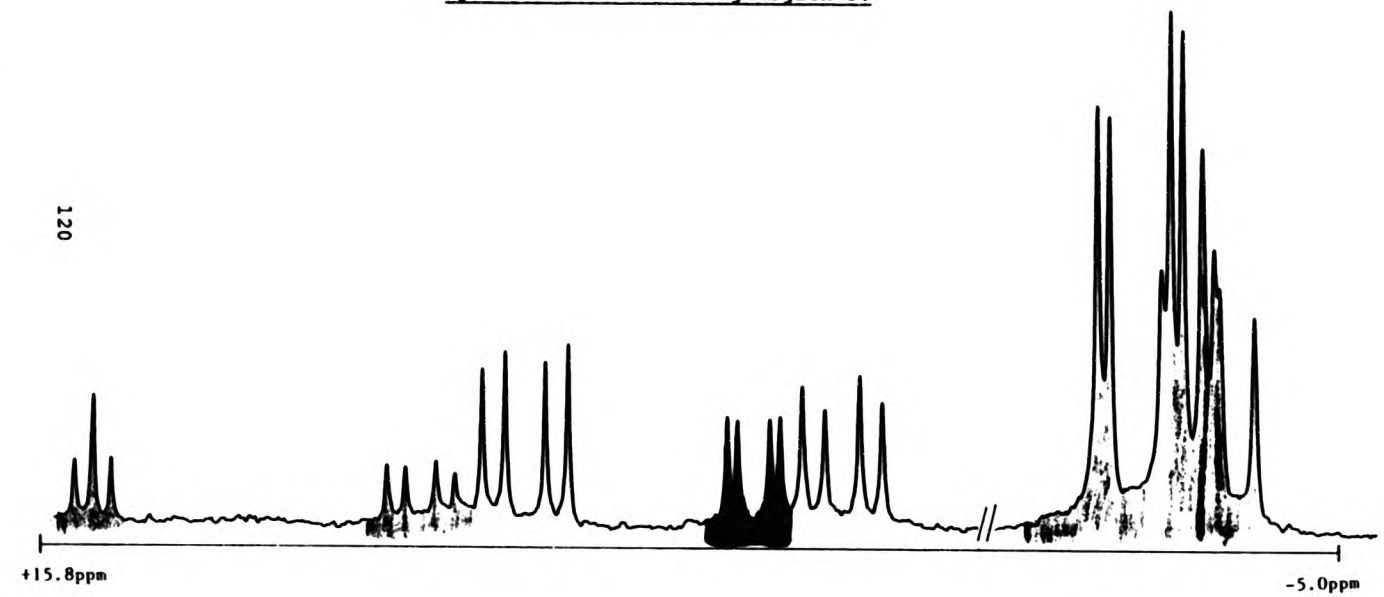
Spectrum 3.2. : Showing Region 1.



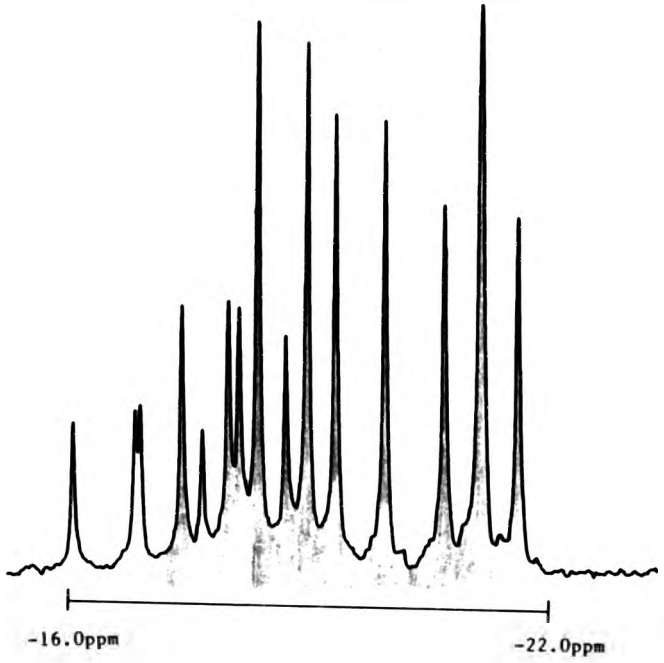
Spectrum 3.2. : Showing Region 2.



Spectrum 3.2. : Showing Region 3.



Spectrum 3.2. : Showing Region 4.



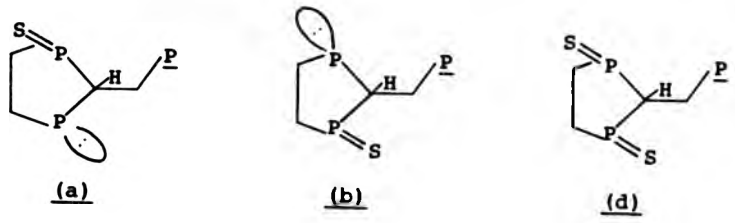


Fig. 3.4. : Showing the relevant phosphorus atom of the sulphurised species whose resonances are observed in Region 4.

(2) REGION 3.

The resonances observed between $\delta(P)$ = +15.8ppm and $\delta(P)$ = -5.0ppm are found to include those arising from P_A and P_M of unsulphurised (IX). Consequently, it is presumed that the remainder of these resonances arise from unsulphurised ring phosphorus atoms, species (a), (b), (c), (e) and (f) in Figure 3.3. The relevant phosphorus atoms are indicated in Figure 3.5.

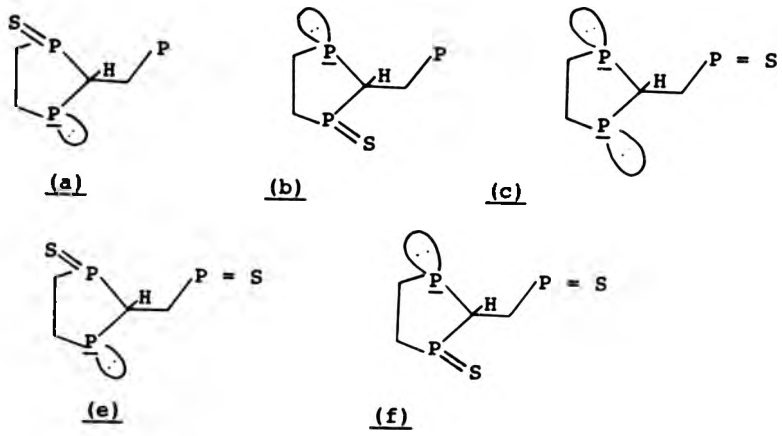


Fig. 3.5. : Showing the relevant phosphorus atom of the sulphurised species whose resonances are observed in Region 3.

(3) REGION 1.

The sets of resonances at the high frequency phosphorus (V) region between δ(P) = +76.0ppm and δ(P) = +57.0ppm, are assumed to arise from the ring phosphorus atoms i.e. species (a), (b), (d), (e), (f) and (g) for reasons explained later. The relevant phosphorus atoms are indicated in Figure 3.6.

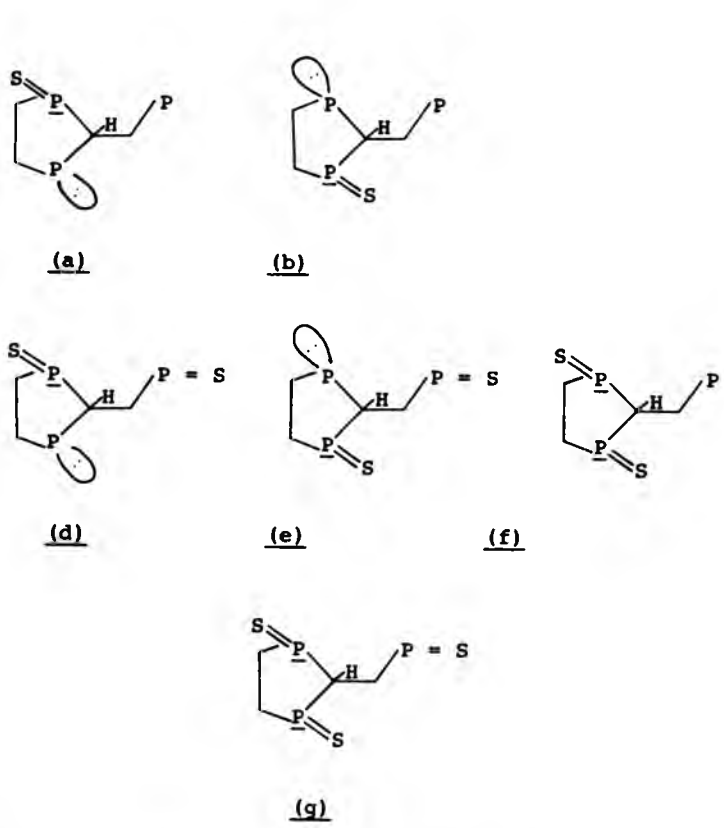


Fig. 3.6. : Showing the relevant phosphorus atom of the sulphurised species whose resonances are observed in Region 1.

(4) REGION 2.

The final set of resonances between δ(P) = +43.5ppm and δ(P) = +40.0ppm also arise from sulphurised phosphorus atoms, and taken to arise from all those species where the exocyclic phosphorus atom is sulphurised, i.e. species (c), (e), (f), and (g). The relevant phosphorus atoms are indicated in Figure 3.7.

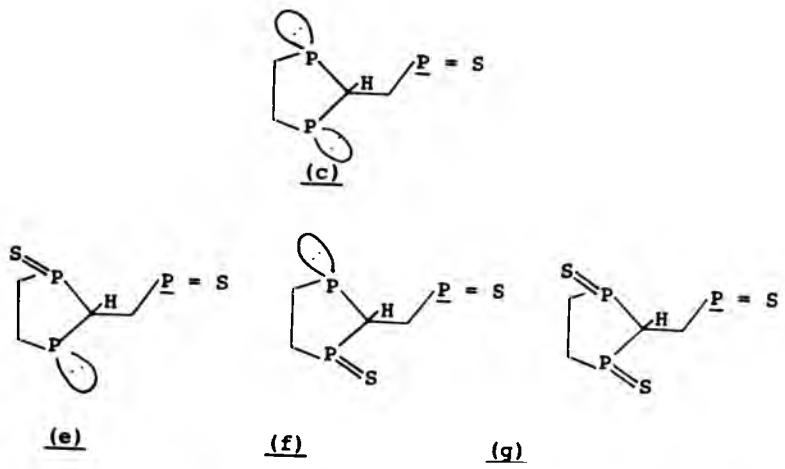


Fig. 3.7. : Showing the relevant phosphorus atom of the sulphurised species whose resonances are observed in Region 2.

The total assignment of the seven different spin systems was conducted using the sample containing two equivalents of sulphur (Spectrum 3.2.), since all the different species were observed (Fig. 3.3). Other samples containing additional half equivalents of sulphur, to full sulphurisation, were also investigated as they permitted

resonance 'intensity monitoring' of the different species present and hence aided assignments.

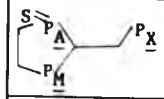
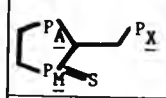
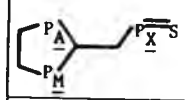
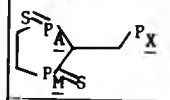
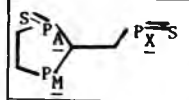
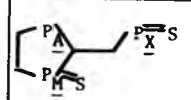
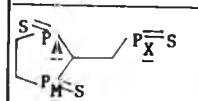
The analysis of all the spectra obtained at each step from further addition of half equivalents of sulphur, involved great care being taken due to the presence of so many spin systems, as resonances appeared very close together resulting in overlapping in some cases. By the use of enough data points and very careful measurement of the coupling constants, the slight variations in the values allowed for differentiation between the resonances and hence, the complete assignment for each sulphurised species of (IX). As there was no excessive overlapping of the resonances, it was not necessary to conduct a two-dimension experiment.

In Spectrum 3.2., each set of related resonances for a particular spin system has been given the same colour code. Table 3.1. was subsequently constructed, such that each sulphurised species (i.e. spin system) was drawn using the same colour code.

Three spin systems have been chosen to illustrate the steps taken in the spectral analysis and on examination, first order AMX and second order ABX type spin systems can be recognised.

(A) The first example taken is the resonances coloured red in Spectrum 3.2. The ^{31}P n.m.r. spectrum recorded from a sample containing a ratio of half an equivalent of sulphur to one equivalent of (IX), shows this set of well-defined, intense, resonances which are thought to arise from a monosulphurised species. They

Table 3.1.: ^{31}P n.m.r. data for the seven sulphurised species of triphosphine (IX).

SULPHURISED SPECIES	(a),(b) CHEMICAL SHIFT, δ, ppm			COUPLING CONSTANT, J, Hz		
	(P_A)	$(P_{B/M})$	(P_X)	$^2J(P_A\text{-}P_{B/M})$	$^3J(P_A\text{-}P_X)$	$^3J(P_{B/M}\text{-}P_X)$
 (a)	+66.2	-3.5	-19.2	6.7	25.6	40.3
 (b)	-4.5	+62.7	-17.9	22.6	23.8	29.0
 (c)	+15.3	+10.3	+42.4	10.4	10.1	27.2
 (d)	+60.8	+57.3	-21.4	30.8	18.3	19.2
 (e)	+75.5	-4.5	+40.6	48.2	9.8	0.0
 (f)	+5.2	+67.0	+42.9	23.8	5.8	30.5
 (g)	+63.3	+62.3	+42.1	30.5	15.8	23.8

NOTES OVERLEAF

NOTE

(a) Chemical shifts relative to external 85% H_3PO_4.

(b) In C_6H_6/C_6D_6 at 25°C.

(c) ^{31}P n.m.r. data for the free triphosphine (IX) in C_6H_6/C_6D_6 at 25°C.

Chemical shifts relative to 85% H_3PO_4.

$\delta(P_A)$ = +8.7ppm, $\delta(P_M)$ = +3.9ppm and $\delta(P_X)$ = -16.5ppm

Coupling constants.

$^2J(P_A\text{-}P_M)$ = 12.8Hz, $^3J(P_A\text{-}P_X)$ = 36.0Hz and $^3J(P_M\text{-}P_X)$ = 36.0Hz

form a first order AMX spin system, where δ(P) = +66.2ppm (sulphurised cyclic phosphorus), δ(P) = -3.5ppm (unsulphurised cyclic phosphorus) and δ(P) = -19.2ppm (unsulphurised exocyclic phosphorus). The three coupling constants measured are $^{2}J(P_A\text{-}P_M)$ = 6.7Hz, $^{3}J(P_{A/M}\text{-}P_X)$ = 25.6Hz and $^{3}J(P_{A/M}\text{-}P_X)$ = 40.3Hz. Thus, these resonances must arise from species (a) or (b).

Similar considerations also apply the resonances coloured purple, which are assigned to species (b), with the red resonances assigned to species (a) and can be taken to be a diastereoisomeric pair. Since the chemical shift positions for the red and purple resonances are very similar they cannot be differentiated from each other, thus the assignments with respect to species (a) and (b) are arbitrary. However, $^{2}J(P^{III}\text{-}P^{V})$ differ significantly from each other for species (a) and (b) (Table. 3.1), which will be explained later.

(B). The next example taken is of those resonances coloured green in Spectrum 3.2., which arise from a second order ABX spin system. The resonances from the AB part of the spectrum are at $\delta(P_A)$ = +60.9ppm and $\delta(P_B)$ = +57.3ppm (Region 1) and consist of an eight-line pattern which, on quasi first order analysis yields $^{2}J(P_A\text{-}P_B)$ = 30.8Hz, $^{3}J(P_A\text{-}P_X)$ = 19.2Hz and $^{3}J(P_B\text{-}P_X)$ = 18.3Hz. The fact that these resonances occur in the phosphorus (V) region of the spectrum and that they are shifted by about +50.0ppm from the free ligand, indicates that both of the ring phosphorus atoms are sulphurised.

The exocyclic P_X nucleus resonance is found in the phosphorus (III) region of the spectrum at $\delta(P_X) \approx$ -21.4ppm, indicating the phosphorus atom to be unsulphurised. These resonances are observed as a 'simple triplet', showing some second-order character where the two values of $^3J(P^V\text{-}P^V)$ are 18.9Hz and 18.6Hz. Thus these signals must arise from species (d). In order to get more precise values of the parameters a fuller analysis was undertaken as follows.

11,12

ANALYSIS BY CALCULATION OF THE AB PART OF THE SPECTRUM, OF SPECIES (d) WITH RESPECT TO FORM (i) IN FIGURE 3.8

STEP 1. Calculation of the Average chemical shift position in hertz.

(Line 1 + 4)/2 = 2151.8 Hz. = δ Avg.

(Line 1 + 4)/2 = 2133.1 Hz. = δ Avg.

STEP 2. Calculation of the Effective chemical shift position in Hz. i.e. δ_{Eff_A}, δ_{Eff_B}.

δ_{Eff_A}, δ_{Eff_B}

$Eff_A = [\ \delta$ Avg.$+ (1/2\ \nu_o \delta_{AB})]$Hz. .....EQUATION 3.1.

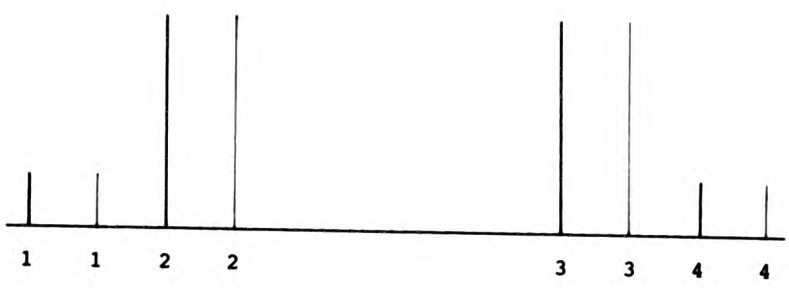
$Eff_B = [\ \delta$ Avg.$+ (1/2\ \nu_o \delta_{AB})]$Hz. .....EQUATION 3.2.

$\nu_o \delta_{AB}$ is the chemical shift difference between the A and B nuclei which is given by:

$$\nu_o \delta_{AB} = [(1\text{-}4).(2\text{-}3)]\text{Hz}.$$

The results obtained from the evaluation of the Equations 3.1. and 3.2. are as follows:

FORM (i)



FORM (ii)

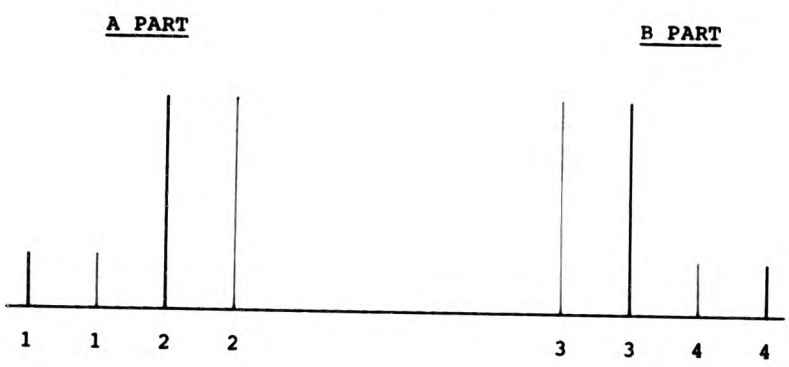


Fig. 3.8. : Schematic representation of the AB part of the spectrum of species (d). Here, either FORM (i) where the relative signs of $^{3}J(P_{A}-P_{X})$ and $^{3}J(P_{B}-P_{X})$ are the SAME; or FORM (ii), where the relative signs of $^{3}J(P_{A}-P_{X})$ and $^{3}J(P_{B}-P_{X})$ are OPPOSITE, depicts the true eight-line pattern of the sulphurised species (d).

TABLE 32

PAGINATION ERROR

δ_{Eff_A} = 2214.5 Hz. δ_{Eff_A} = 2195.2 Hz.

δ_{Eff_B} = 2089.1 Hz. δ_{Eff_B} = 2071.0 Hz.

STEP 3. The actual chemical shift frequency $\delta(P_A)$ and $\delta(P_B)$ and the coupling constants $^3J(P_A-P_X)$ and $^3J(P_B-P_X)$ can be calculated using Equations 3.3. - 3.6., and the results obtained in Step 2.

$$\delta_{Eff_A} = \delta(P_A) + 1/2\ {}^3J(AX)\ \text{Hz.} \quad \text{....EQUATION 3.3.}$$

$$\delta_{Eff_A} = \delta(P_A) - 1/2\ {}^3J(AX)\ \text{Hz.} \quad \text{....EQUATION 3.4.}$$

where, $\delta_{Eff_A} - \delta_{Eff_A} = {}^3J(AX)$ Hz.

and

$$\delta_{Eff_B} = \delta(P_B) + 1/2\ {}^3J(BX)\ \text{Hz.} \quad \text{....EQUATION 3.5.}$$

$$\delta_{Eff_B} = \delta(P_B) - 1/2\ J(BX)\ \text{Hz.} \quad \text{....EQUATION 3.6.}$$

where, $\delta_{Eff_B} - \delta_{Eff_B} = {}^3J(BX)$ Hz.

The results obtained from the evaluation of these Equations are tabulated below.

Table 3.3. : The calculated and measured ^{31}P n.m.r. data for species (d) with respect to Form (i).

	FREQUENCY IN Hz.				
	$\delta(P_A)$	$\delta(P_B)$	$^2J(AB)$	$^3J(AX)$	$^3J(BX)$
CALCULATED	2204.9	2080.1	30.8	19.3	18.1
MEASURED	2206.6	2078.1	30.8	19.2	18.3

$^2J(P_A-P_B)$ can be measured directly from the spectrum; it is the frequency difference between lines 1-3, 2-4, 5-7 or 6-8.

This AB analysis based on Form (i) shows good correlation with the parameters measured directly from the spectrum.

ANALYSIS OF THE X PART OF THE SPECTRUM WITH RESPECT TO FORM (i).

Theoretically the X part of an ABX spin system consists of a six-line pattern (Fig. 3.9).

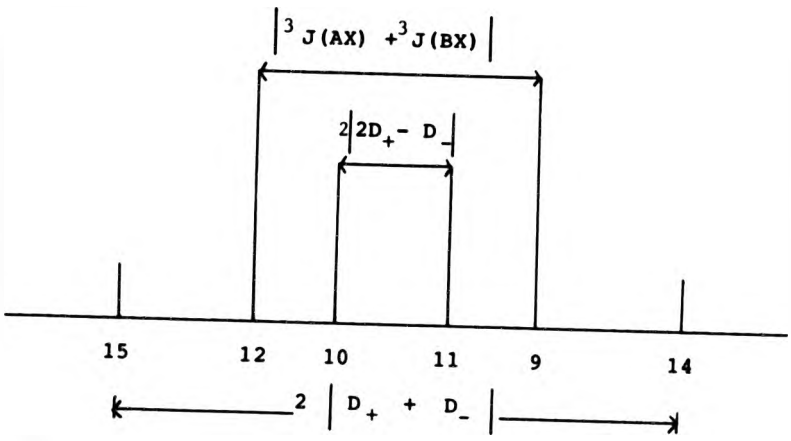


Fig. 3.9 : Theoretical representation of the X part of an ABX spin system.

The X part of the actual spectrum obtained for this ABX spin system is observed as a 'deceptively simple'

1:2:1 triplet. Frequently, fewer lines are observed in the X part of the spectrum, according to the value of $\left|{}^3J(AX)-{}^3J(BX)\right|$. Deceptively simple 1:2:1 triplets occur either because the spectrum is a deceptively simple A_2X spin system, or because $J(AX) \approx J(BX)$, with the relative signs of the two coupling constants being the same.

The positive quantities D_+ and D_- (Fig. 3.9) can be calculated by the respective use of Equations 3.7. and 3.8. employing values obtained previously from the AB calculations, where the relative signs of the coupling constants ${}^3J(AX)$ and ${}^3J(BX)$ are the same. By making $\left|{}^3J(BX)\right|$

$$D_+ = \{[1/2\ \nu_o \sigma_{AB} + 1/4(J(AX)-J(BX))]^2 + 1/4\ \ J(AB)\}^{\frac{1}{2}}$$

....EQUATION 3.7.

$$D_- = \{[1/2\ \nu_o \delta_{AB} - 1/4(J(AX)-J(BX))]^2 + 1/4\ \ J(AB)\}^{\frac{1}{2}}$$

....EQUATION 3.8.

$$\nu_o \delta_{AB} = \delta(P_A) - \delta(P_B)\,Hz.$$
$$= 2204.9-2080.1 = 124.8Hz.$$

positive in Equation 3.7. and 3.8., values for D_+ and D_- can be calculated when the relative signs of the coupling constants ${}^3J(AX)$ and ${}^3J(BX)$ are the opposite. The results obtained are shown in Table 3.4.

Table 3.4. : The calculated values for the positive quantities D+ and D - with respect to Form (i).

	D_+(Hz)	D_- (Hz)
RELATIVE SIGNS OF $^3J(AX)$ AND $^3J(BX)$ ARE THE SAME.	64.6	64.0
RELATIVE SIGNS OF $^3J(AX)$ AND $^3J(BX)$ ARE OPPOSITE.	73.4	55.2

The values for D_+ and D_- can also be measured directly from the AB part of the spectrum, when the following frequencies are subtracted:

$2D_+$ = Lines(8-4) = (7-3)Hz.

D_- = 64.6Hz. = 64.6Hz.

and $2D_+$ = Lines(5-1) = (6-2)Hz.

D_- = 64.0Hz. = 64.0Hz.

The measured values correlate with the calculated values, when it is taken that the relative signs of the coupling constants $^3J(AX)$ and $^3J(BX)$ are the same.

The measured values for the separation of the lines in the X part of the spectrum are 18.9Hz and 18.6Hz Using the calculated values from the AB and X parts of the spectrum, the frequency separation between the possible six lines of the X part of the spectrum can be obtained,

as shown in Table 3.5.

Table 3.5. : Presenting calculated values for the frequency separation between the six possible resonances at the X part of the spectrum.

LINE No.		FREQUENCY SEPARATION IN Hz.	
		RELATIVE SIGNS OF $^3J(AX)$ AND $^3J(BX)$	
		(i) THE SAME $D_+=64.6$, $D_-=64.0$	(ii) OPPOSITE $D_+=73.4$, $D_-=55.2$
9	$\nu_x - 1/2(JAX + JBX)^*$	-18.7	+0.6
10	$\nu_x + D_+ - D_-$	+0.6	-18.2
11	$\nu_x - D_+ + D_-$	-0.6	+18.2
12	$\nu_x + 1/2(JAX + JBX)^*$	+18.7	-0.6
13	$2\nu_o - \nu_x$	0.0	0.0
14	$\nu_x - D_+ - D_-$	-128.6	+128.6
15	$\nu_x + D_+ + D_-$	+128.6	-128.6

NOTE.

(a). It is taken that $\nu_x = 0.0$Hz.

(b). *=Calculated values used for:

$^3J(AX) = 19.3$Hz and

$^3J(BX) = 18.1$Hz.

(c). Values are given using the calculated values for D_+ and D_-.

The calculations were then repeated for the AB part of the spectrum with respect to Form (ii) shown in Figure 3.8, where the relative signs of the coupling constants $^3J(P_A\text{-}P_X)$ and $^3J(P_B\text{-}P_X)$ are opposite. The results obtained are presented below in Tables 3.6., 3.7. and 3.8.

Table 3.6. : The calculated and measured ^{31}P n.m.r. data for species (d) with respect to Form (ii).

	FREQUENCY IN Hz.				
	$\delta(P_A)$	$\delta(P_B)$	$^2J(AB)$	$^3J(AX)$	$^3J(BX)$
CALCULATED	2204.8	2089.5 2080.1	30.8	19.7	-18.9
MEASURED	2206.6	2078.1	30.8	19.2	18.3

Tabulated results for the X part of the spectrum.

Table 3.7. : The calculated and measured values for the positive quantities D+ and D- with respect to Form (ii).

CALCULATED VALUES	D_+ (Hz)	D_- (Hz)
RELATIVE SIGNS OF $^3J(AX)$ AND $^3J(BX)$ ARE THE SAME.	71.3	52.7
RELATIVE SIGNS OF $^3J(AX)$ AND $^3J(BX)$ ARE OPPOSITE.	62.0	61.8
MEASURED VALUES	54.9	73.6

Table 3.8. : Presenting calculated values for the frequency separation between the six possible resonances at the X part of the spectrum.

LINE No.		FREQUENCY SEPARATION IN Hz.	
		RELATIVE SIGNS OF $^3J(AX)$ AND $^3J(BX)$	
		(i) THE SAME $D_+=71.3$, $D_-=52.7$	(ii) OPPOSITE $D_+=62.0$, $D_-=61.8$
9	$\nu_x - 1/2(JAX+JBX)^*$	-0.4	+19.3
10	$\nu_x + D_+ - D_-$	+18.6	-0.2
11	$\nu_x - D_+ + D_-$	-18.6	+0.2
12	$\nu_x + 1/2(JAX+JBX)^*$	+0.4	-19.3
13	$2\nu_o - \nu_x$	0.0	0.0
14	$\nu_x - D_+ - D_-$	-124.0	+123.8
15	$\nu_x + D_+ + D_-$	+124.0	-123.8

NOTE.

(a). It is taken that ν_x = 0.0Hz.

(b). *=Calculated values used for:

$^3J(AX)$ = 19.7Hz and

$^3J(BX)$ = -18.9Hz.

(c). Values are given using calculated values for D_+ and D_-.

The foregoing analyses all relate to species in which the exocyclic phosphorus atom remains unsulphurised and thus demonstrates that the chemical shift of the sulphurised cyclic phosphorus atoms is above +55ppm. Thus, Region 2 must correspond to sulphurised exocyclic phosphorus atoms.

The values calculated from the AB and X parts of the spectrum, show that there is no correlation between the parameters, with respect to Form (ii).

Thus, the results of these calculations confirm that this is an ABX spin system, where the relative signs of the coupling constants $^{3}J(P_{A}-P_{X})$ and $^{3}J(P_{B}-P_{X})$ are the same, as is reasonable for species (d).

(C). The final example is the set of resonances coloured dark blue in Spectrum 3.2., which arise from a first order AMX spin system. The three relative chemical shift positions are $\delta(P)$ = +75.5ppm (Region 1.), $\delta(P)$ = -4.5ppm (Region 3.) and $\delta(P)$ = +40.6ppm (Region 2.).

At $\delta(P)$ = +75.5ppm, a 'doublet of doublets' is observed with couplings of 48.2Hz and 9.8Hz. This set of resonances, occurring in the phosphorus (V) region, indicates the presence of a sulphurised cyclic phosphorus atom.

The resonances at $\delta(P)$ = -4.5ppm indicate the presence of an unsulphurised cyclic phosphorus atom, a 'simple doublet' is observed with a coupling of 48.2Hz; the total intensity is approximately the same as that of the resonances at $\delta(P)$ = +75.5ppm. The presence of a 'simple

doublet' suggests that one of these coupling constants is zero.

The resonances at δ(P) = +40.6ppm indicate the presence of a sulphurised exocyclic phosphorus atom, a 'simple doublet' is again observed with a coupling of 9.8Hz. The P_X part of the spectrum would be expected to show a 'doublet of doublets' with couplings from $^3J(P_A-P_X)$ and $^3J(P_M-P_X)$. Thus, one of the ^3J(P-P) couplings has a value of 9.8Hz and the other 0.0Hz.

Hence, the recurring coupling of 48.2Hz measured, are taken to arise from the cyclic phosphorus atoms that is $^2J(P_A-P_M)$ = 48.2Hz.

This species contains one cyclic and one exocyclic sulphurised phosphorus atom, and also an unsulphurised cyclic phosphorus atom, corresponding to species (e) or (f).

Similarly, it follows that the AMX spin system marked by the grey colour which also gives resonances in Regions (4), (3), and (2), must be the other member of the (e)/(f) pair. It is interesting to note that whereas the (a)/(b) pair of diastereoisomers were formed in substantially different amounts, approximately equal proportions of species (e) and (f) are present in the mixture, even though the relationship between this pair of diastereoisomers is the same as that between species (a) and (b).

Finally, the remaining resonances in the Regions (3) and (4) must be assigned to the fully sulphurised species (g) and indeed their pattern corresponds exactly with an authentic sample of (g), isolated in a separate experiment.

The spin systems relating to all seven sulphurised species have been identified from the spectra obtained at 36.2MHz, with the two measurable n.m.r. parameters comparable to those measured from the spectra recorded at 24.2MHz. The two n.m.r measurable parameters found have been presented in Table 3.1.

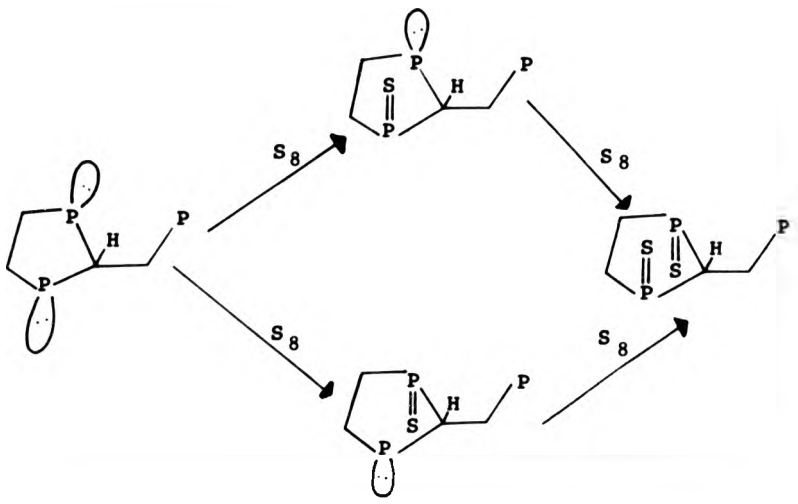
The mechanism by which sulphurisation is thought to occur involves retention of configuration at the phosphorus atom. However, reaction products possible upon sulphurisation of the ring phosphorus atoms either, with (1) inversion or, with (2) retention of configuration are shown in Figure 3.10.

Observations of Figure 3.10. show that for the two monosulphurised products obtained with inversion of configuration, at the phosphorus atom, the P=S group and the lone pair of electrons are similarly orientated; whilst with retention of configuration, the two groups are orientated in directions opposite to each other. The disubstituted species formed by inversion and retention are enantiomeric, and hence are indistinguishable by phosphorus n.m.r. spectroscopy.

If both mechanisms occurred simultaneously, the two reaction schemes shown in Figure 3.11. would also be feasible. Following these reaction schemes, four different monosubstituted products would be predicted.

The disubstituted species formed by the schemes shown in Figure 3.11. are all in the 'cis' form, and related as 1≡3 and 2≡4.

(1). INVERSION OF CONFIGURATION.



(2). RETENTION OF CONFIGURATION.

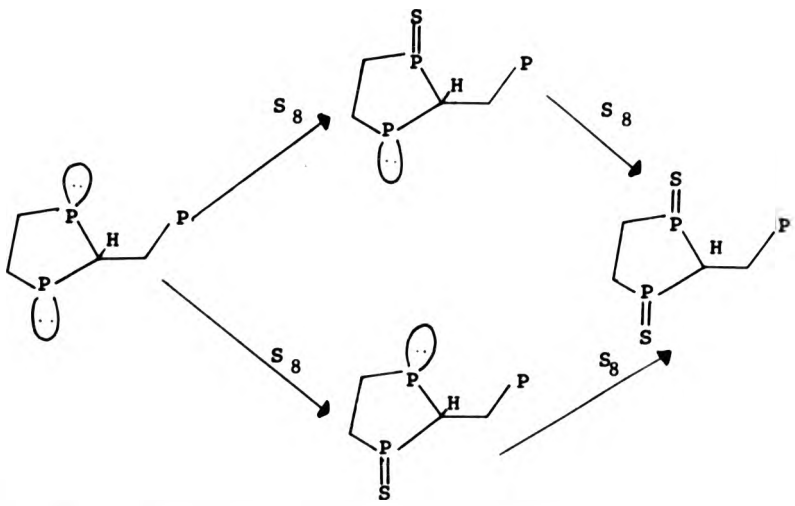


Fig. 3.10. : Diagrammatic representation of the two possible mechanisms by which sulphurisation of (IX) can proceed.

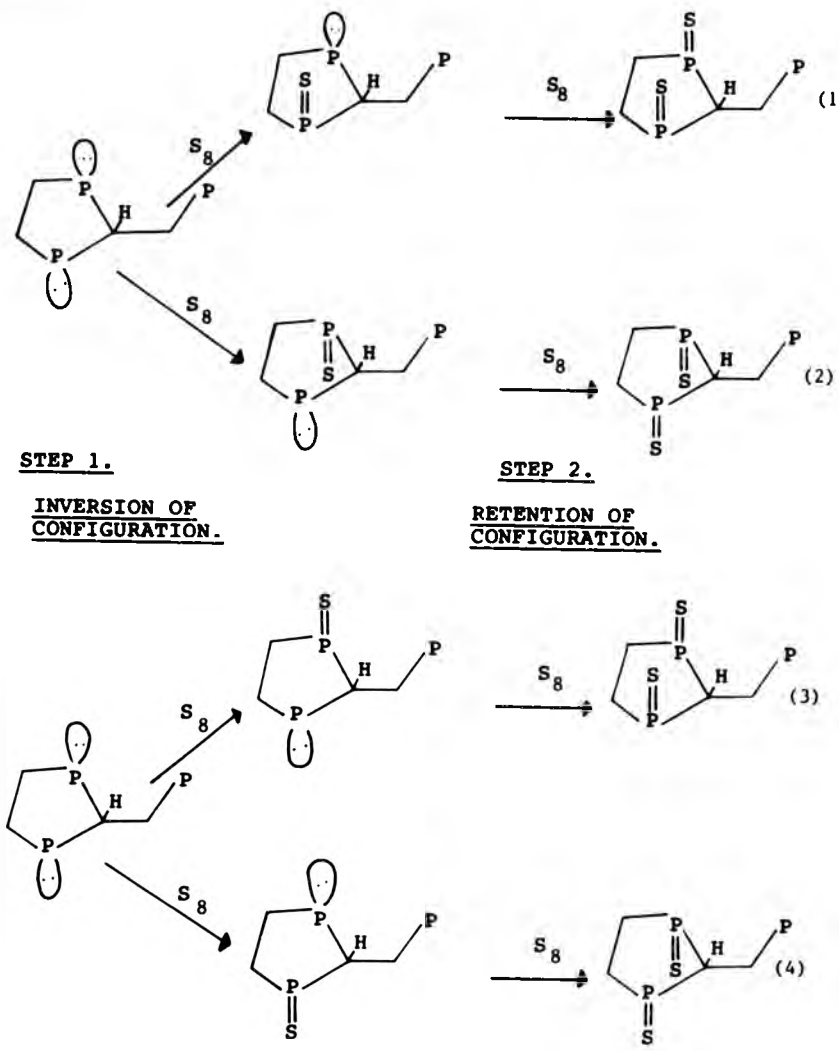


Fig 3.11. : Diagrammatic representation of the sulphurisation of (IX) occurring simultaneously with inversion and retention of configuration, and vice versa.

If both mechanisms were in operation, the reaction schemes shown in Figures 3.10. and 3.11. would all be expected. Thus, the expected number of monosubstituted and disubstituted species would be four in each case. However from the analysis of the ^{31}P n.m.r. spectra obtained (described previously), only two of each type of sulphurised species are actually observed.

If only one of the reaction mechanisms was in operation, two monosubstituted and two disubstituted products would be predicted. This is consistent with the observations and thus it can be taken that the sulphurisation proceeds by only one of the reaction mechanisms. From previous work conducted on sulphurisation of phosphines, it seems reasonable to assume that the reaction occurs by retention of configuration alone.

The magnitudes of $^{n}J(P^{III}-P^{III})$ over two or three bonds are generally conformationally dependent.[13-16] In the parent species (IX) $^{2}J(P_{A}-P_{M})$ = 12.8Hz which is similar to its value of 10.1Hz in species (c), suggests that sulphurisation of the exocyclic phosphorus atom does not affect this coupling constant to any great extent. This is reasonable since such sulphurisation would not be expected to affect the ring conformation very much. The same conclusion can be reached by comparing $^{2}J(P^{V}-P^{V})$ in species (d) and (g), although in this case it should be borne in mind that $(P^{V}-P^{V})$ are not affected by conformational changes to any great extent.[1,9]

It is reasonable to suppose that the exocyclic phosphorus atom bears a different conformational relationship

to each of the cyclic phosphorus atoms in all of these species and this can then account for the large variations observed in the couplings $^{3}J(P_{A}^{III}-P_{X}^{III})$ and $^{3}J(P_{M}^{III}-P_{X}^{III})$. For example $^{3}J(P_{A}^{III}-P_{X}^{III})$ in species (b) is substantially smaller than the corresponding coupling $^{3}J(P_{M}^{III}-P_{X}^{III})$ in species (a), and similar considerations apply to species (e) and (f) including, perhaps surprisingly, the $^{3}J(P^{V}-P^{V})$ in species (e) and (f). That is, there appear to be substantial imbalances in the conformational populations of different diastereoisomers and these may be related to a tendency of the lone pairs of electrons on the phosphorus atoms to be in proximate positions.

However, it is much less clear why there should be substantial differences in the <u>trans</u> cyclic coupling $^{2}J(P_{A}-P_{M/B})$ within the pairs of species (a)/(b) and (e)/(f), since changes in the conformational position of the exocyclic phosphorus atom should apparently have little affect upon the spacial relationship of $(P_{A}-P_{M})$. So far it has been tacitly assumed that these five-membered rings are effectively planar.

Using molecular models it is found that the five-membered ring is not perfectly planar and is in fact likely to bend about the a notional phosphorus-phosphorus link (five-membered rings such as $(PPh)_{5}$ are usually found to adopt an envelope-shaped conformation,[5,17] at least in the solid state) and this bending allows for two conformations to exist (Fig. 3.12).

In both conformations (I) and (II), the dihedral angle S/P/P/Ph or lone pair/P/P/Ph, is 0°and therefore it

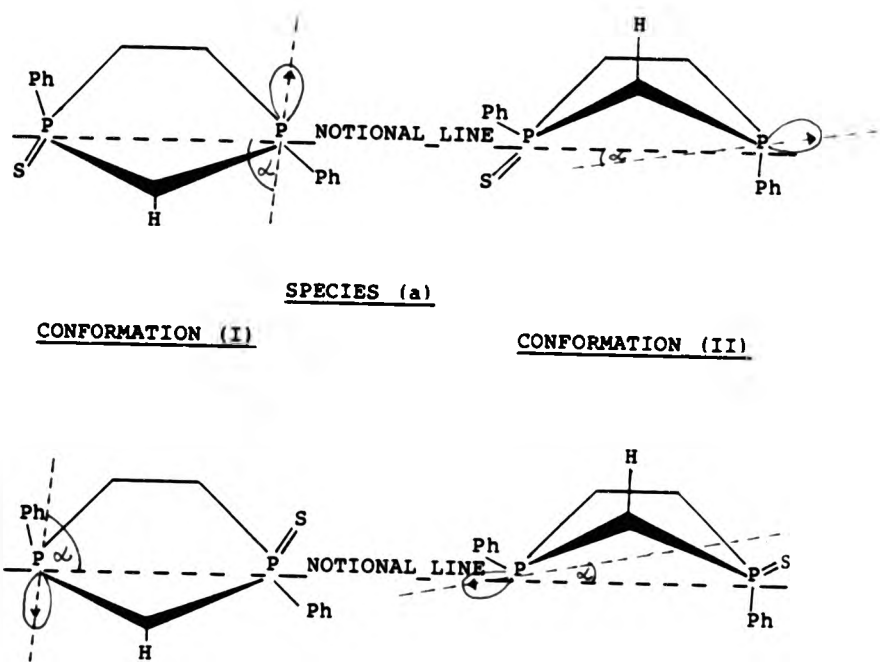
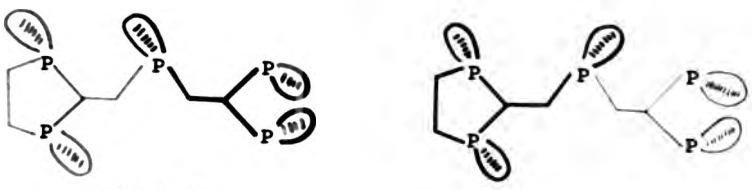


Fig. 3.12 : Diagrammatic representation of species (a) and (b) showing the bend about the phosphorus-phosphorus bond, allowing for Conformations (I) and (II) to exist.

might be thought that the relative behaviour of the two (P-P) coupling constants would be unaffected. It is also necessary to consider the skew angle α, which relates the direction of the phosphorus lone pair of electrons to the other phosphorus. In conformation (I) in species (a) this angle is ca 70° and the lone pair is not fully directed away from the other phosphorus atom. Whereas in conformation (II) the skew angle is ca 15°, and the lone pair direction is almost completely opposed in the other direction. The values of $^2J(P\text{-}P)$ in the two conformations might well be different and therefore the observed value of the coupling will be a weighted average, which depends upon the relative populations of the two conformers.[18] Similar considerations apply to species (b). The factors determining the relative populations of the two conformers are complex, but are likely to include the bulk and conformational preference of the exocyclic phosphorus atom, whilst the lone pair may well interact preferentially with one or the other of the cyclic phosphorus atoms. Whatever the detailed nature of these factors, they are likely to be similar for conformation (I) of species (a) and conformation (II) of species (b), and similarly for conformation (II) of species (a) and conformation (I) of species (b). Thus, if it happens that for species (a) (I) is the predominant conformation, then it will be (II) for species (b). As pointed out above, these two conformations can be expected to give rise to different values to $^2J(P^V\text{-}P^{III})$ and hence there will be different values observed for $^2J(P^V\text{-}P^{III})$ for these two species.

^{31}P N.M.R. SPECTRAL ANALYSIS OF THE SULPHURISATION OF PENTATERTIARY PHOSPHINE (XIII).

The ^{31}P n.m.r. spectral analysis of pentatertiary phosphine (XIII) reveals the presence of two diastereoisomers (Fig. 3.13), which are both found to give a KQXAB spin system, and which are formed in the ratio of 4:1 (discussed in Chapter 2.).

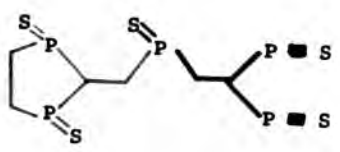


(XIIIa) (XIIIb)

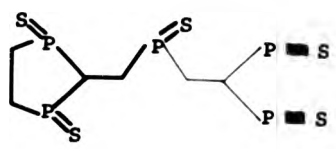
Fig 3.13. : Diagrammatic representation of the two diastereoisomers of (XIII).

For (XIII), there are forty-six possible sulphurised species which can be formulated. For each diastereoisomer, there is the possibility of five mono-, eight di-, seven tri-, four tetra-, and one penta- sulphurised species.

The ^{31}P n.m.r. spectra obtained at 24.2MHz and 36.2MHz, of solutions prepared containing one to four equivalents of sulphur, to one equivalent of (XIII) in benzene show a multitude of spectral resonances, which are not easily analysed (Spectrum 3.3). Therefore, the analysis is based upon the fully sulphurised species of two diastereoisomers (Fig. 3.14 and Spectrum 3.4.).



(XIIIa)



(XIIIb)

Fig. 3.14 : Schematic representation of the fully sulphurised diastereoisomers of (XIII).

The ^{31}P n.m.r. spectrum obtained at 36.2MHz indicates the presence of three major chemical shift regions:-

REGION 1. +64.9ppm to +58.3ppm;

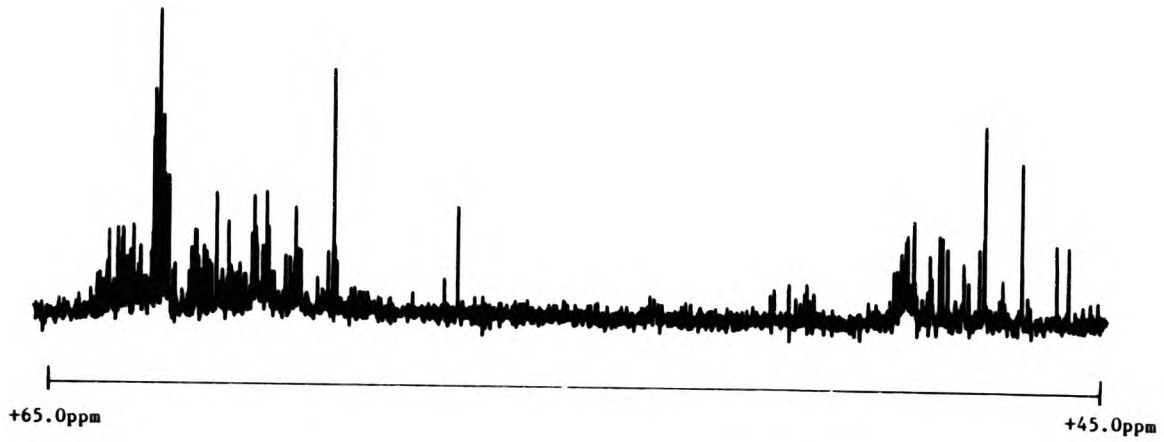
REGION 2. +51.8ppm to +49.6ppm;

REGION 3. +48.2ppm to +44.1ppm.

These three chemical shift regions and their basic pattern of spectral resonances observed are also observed at 24.2MHz, indicating them to be real chemical shift positions.

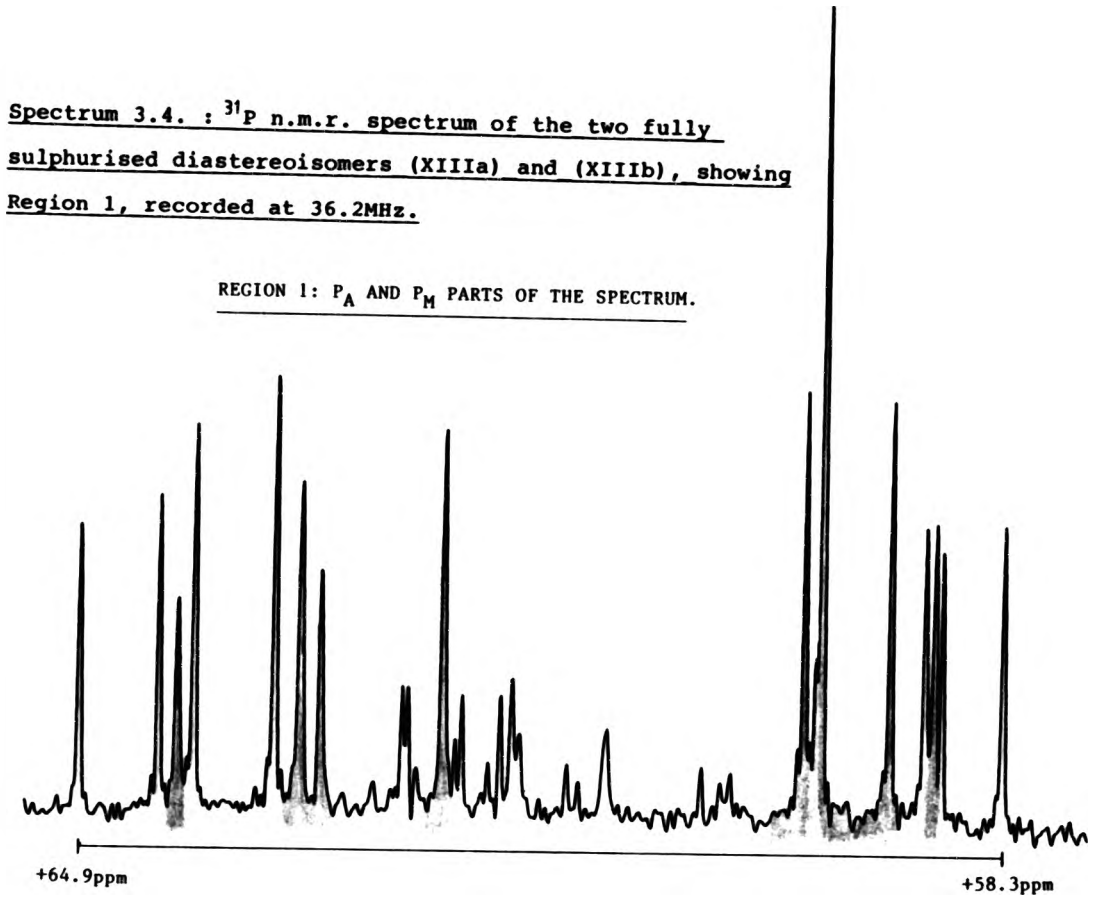
The ^{31}P n.m.r spectrum obtained at 36.2MHz reveals a KQXAB spin system as observed for the free phosphine (XIII). The resonances in the chemical shift Region 1 (from +64.9ppm to +58.3ppm), indicate the presence of four first order three-spin systems. Due to the distortions in intensity of the resonances it is not possible to assign them to the two diastereoisomers, which would be predicted in the 4:1 ratio, as found for the free phosphine (XIII).

Spectrum 3.3. : ^{31}P n.m.r. spectrum of (XIII) containing three equivalents of sulphur, recorded at 36.2MHz.

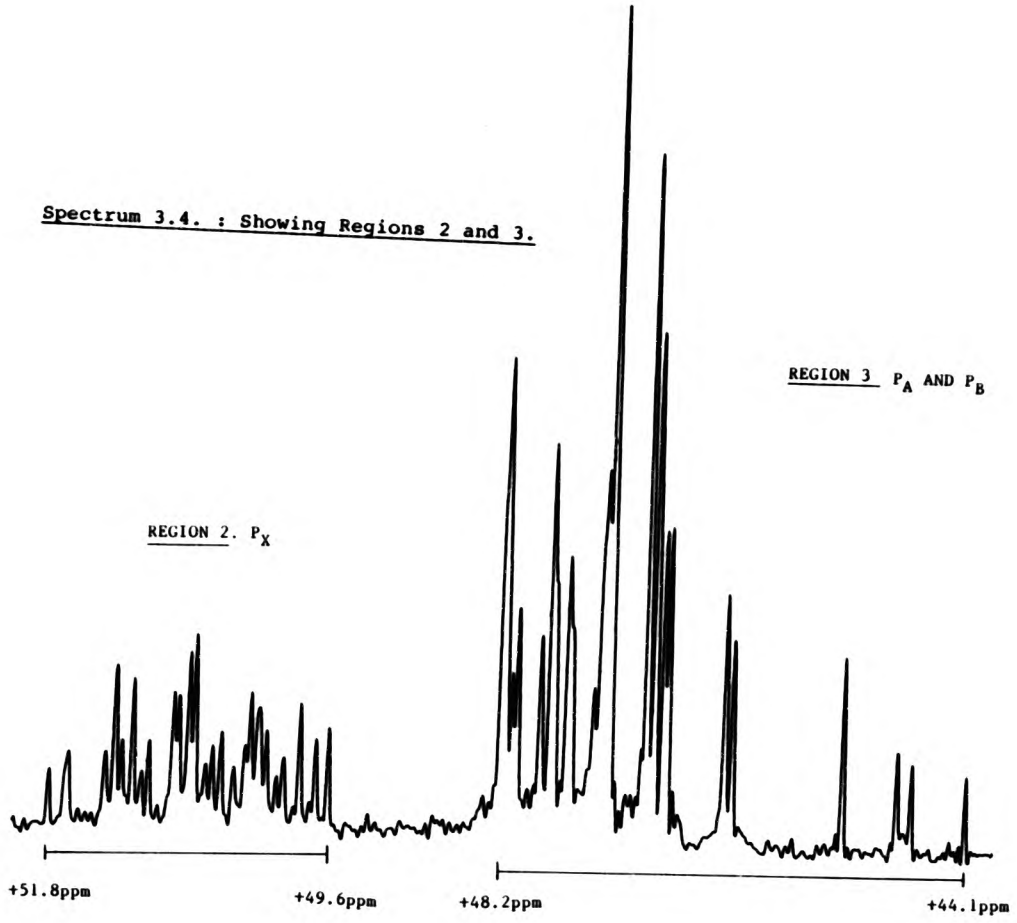


Spectrum 3.4. : ^{31}P n.m.r. spectrum of the two fully sulphurised diastereoisomers (XIIIa) and (XIIIb), showing Region 1, recorded at 36.2MHz.

REGION 1: P_A AND P_M PARTS OF THE SPECTRUM.



Spectrum 3.4. : Showing Regions 2 and 3.



The resonances in this region are taken to arise from the two ring phosphorus nuclei. The four chemical shift positions and coupling constants measured in this region are tabulated in Table 3.9.

Table 3.9. : ^{31}P n.m.r. data obtained from Region 1 for the two fully sulphurised diastereoisomers of (XIII).

LIGAND	CHEMICAL SHIFT δ, ppm.		COUPLING CONSTANT J, Hz.		
	(P_A)	(P_M)	($P_A - P_M$)	($P_A - P_X$)	($P_M - P_X$)
'(XIIIa)'	+63.3	+59.2	29.70	20.75	18.00
'(XIIIb)'	+64.2	+58.9	31.50	36.62	4.58

NOTE.

(a) Chemical shifts relative to external 85% H_3PO_4.

(b) In C_6H_6 /C_6D_6 at 25°C.

From previous investigations on the sulphurisation of polytertiary systems composed of (XIV) (Chapter 2, Section B), it is known that resonances arising from these two sulphurised phosphorus nuclei, (AB), appear in chemical shift Region 3 (+48.2ppm to +44.1ppm), described by an ABX spin system. Thus, it is taken that Region 3 describes the resonances arising from this part of the sulphurised (XIII). The resonances in Region 3 show a high

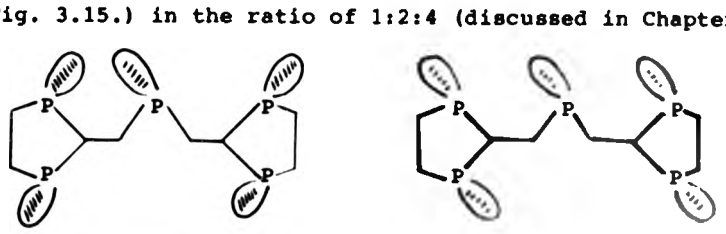
degree of second order character; hence it was not possible to measure any of the n.m.r. parameters for this part of the ligand.

The resonances observed in Region 2 are then taken to arise from couplings to the P_X nucleus in the two diastereoisomers, but as it was not possible to measure the $^3J(P_A-P_X)$ and $^3J(P_M-P_X)$ coupling constants, analysis of the P_X part of the spectrum was not possible.

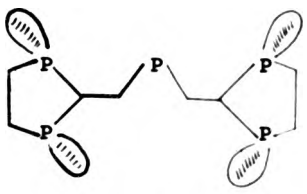
A full analysis of sulphurised (XIII) may have been possible, if a spectrum of the sample could be obtained from a higher field spectrometer.

^{31}P N.M.R. SPECTRAL ANALYSIS OF THE SULPHURISATION OF PENTATERTIARY PHOSPHINE (XII).

The ^{31}P n.m.r. spectral analysis of pentatertiary phosphine (XII) reveals the presence of three diastereoisomers (Fig. 3.15.) in the ratio of 1:2:4 (discussed in Chapter 2.).



(XIIa) (XIIb)



(XIIc/d)

Fig 3.15. : Diagrammatic representation of the three diastereoisomers of (XII).

The total number of possible sulphurised products from all three diastereoisomers which can be formulated are eighty-one. For each diastereoisomer, there are five mono-, ten di-, nine tri-, five tetra-, and one penta-sulphurised species.

The ^{31}P n.m.r. spectra obtained at 24.2MHz and 36.2MHz for samples containing one to four equivalents

of sulphur, to one equivalent of (XII) in benzene, show a multitude of spectral resonances, which could not be completely analysed. Hence, the analysis was based on the fully sulphurised species of the three diastereoisomers. (Spectrum 3.5.).

The ^{31}P n.m.r. spectrum obtained at 36.2MHz reveals the presence of two major chemical shift regions:-

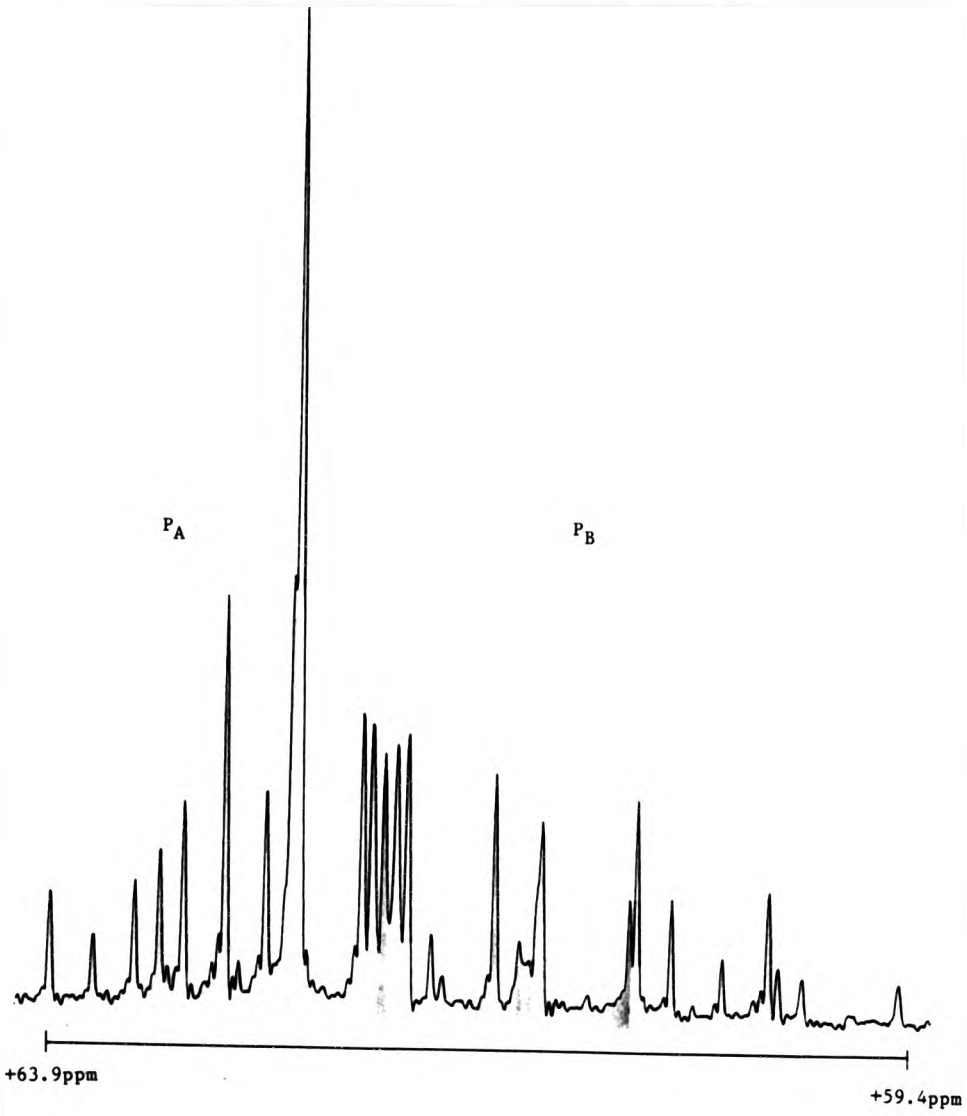
REGION 1. +63.9ppm to +59.4ppm;

REGION 2. +50.6ppm to +46.6ppm.

In Region 1, the presence of two second order AB parts of an AA'BB'X spin system is observed. Although the two sets of AB resonances cannot be assigned to the diastereoisomers from the relative intensities of the resonances, due to distortions, which would be predicted in the ratios observed for the free phosphine; from the configuration of the three diastereoisomers, it would seem reasonable to assume that the two sets of resonances arise from (XIIa) and (XIIb). The ^{31}P n.m.r. parameters obtained from Region 1 are presented in Table 3.10.

The resonances observed in Region 2, are then taken to arise from the couplings to the P_X nucleus. Due to overlapping of resonances, it is not possible to completely analyse this part of the spectrum. However, one set of 'triplet of triplets' are observed, centred at $\delta(P_X)$ = +47.7ppm, with $^3J(P_A-P_X)$ = 15.1Hz. and $^3J(P_M-P_X)$ = 24.9Hz. These values seem to correlate with those obtained at the AB part of the spectrum, for diastereoisomer '(XIIb)'.

Spectrum 3.5. : ^{31}P n.m.r. spectrum of the fully sulphurised diastereoisomers of (XII), showing Region 1.



Spectrum 3.5. : ^{31}P n.m.r. spectrum of the fully sulphurised diastereoisomers of (XII), showing Region 2.

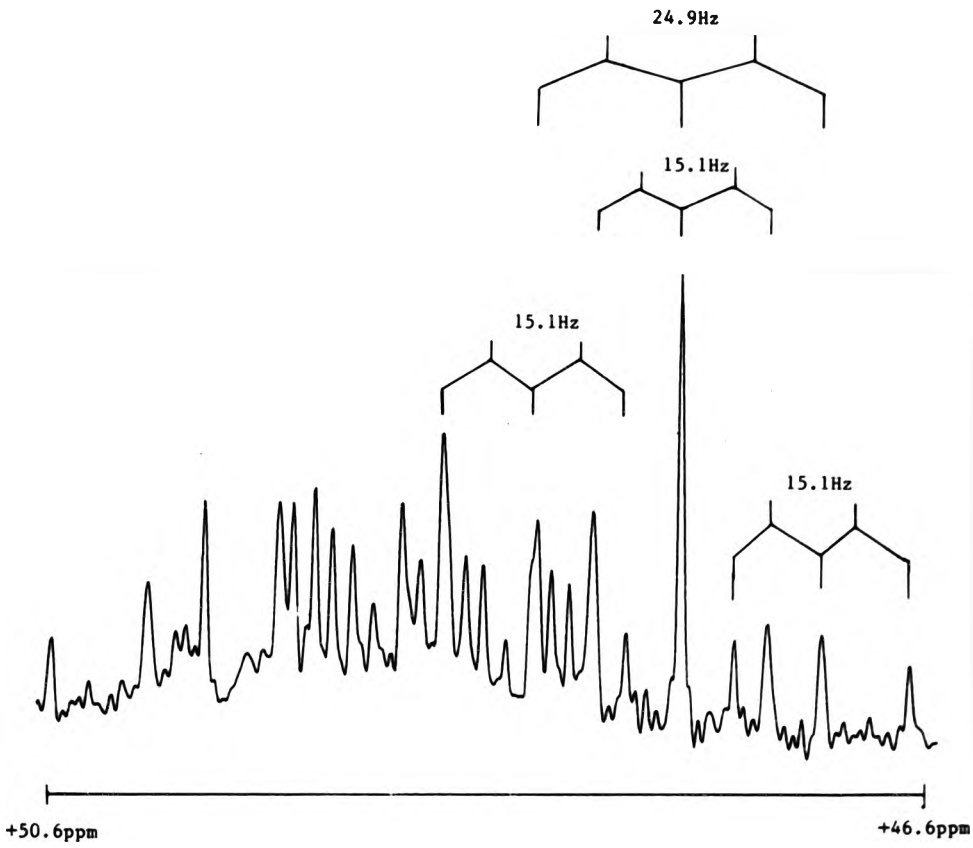


Table 3.10. : ^{31}P n.m.r. data from Region 1. for the fully sulphurised diastereoisomers of (XII).

LIGAND	CHEMICAL SHIFT δ, ppm.		COUPLING CONSTANT J, Hz.		
	(P_A)	(P_M)	(P_A -P_M)	(P_A -P_X)	(P_M-P_X)
'(XIIa)'	+63.2	+60.1	29.90	18.75	22.00
'(XIIb)'	+63.0	+61.0	30.50	15.15	25.50

NOTE.

(a) Chemical shifts relative to external 85% H_3PO_4.

(b) In C_6H_6/C_6D_6 at 25°C.

A full analysis of sulphurised (XII) may have been possible, if a spectrum of the sample could be obtained from a higher field spectrometer.

SUMMARY

From the study of the sulphurisation of these cyclic phosphines, it appears that they have considerable potential for complexation with metal substrates ,as full sulphurisation is possible. However, the number of complexes possible would be less then those formed by sulphurisation, due to the presence of the ring and the trans orientation of the lone pairs of electrons on the ring phosphorus atoms.

The complete assignment of all the sulphurised species of triphosphine (IX) was made easier as it existed in only one form, which reduced the number of potential sulphurised species. Analysis of the pentatertiary phosphines (XII) and (XIII) possessing three and two diastereoisomers respectively produced a vast number of spectral resonances, due to the very large number of possible sulphurised species.

The analysis of the spectra obtained from the sulphurisation of (IX) was achieved by the careful monitoring of the changes in intensity of the resonances and at the same time making accurate measurements of the coupling constants. In this way it was possible to identify related resonances arising from each spin system for every sulphurised species. Using this method, it was observed that;

(1) the exocyclic phosphorus atom was the last to be sulphurised and,

(2) the magnitude of the high frequency shift was from 52ppm to 63ppm.

From the analysis of all the cyclic phosphines, it

is found that the magnitude of the coupling constant $^{2}J(P^{V}-P^{V})$ when both of the ring phosphorus atoms are sulphurised is always ca30Hz.

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CHAPTER 4.

LITHIATED ORGANOPHOSPHORUS COMPOUNDS.

INTRODUCTION.

Lithiated organophosphorus compounds have been widely used as important synthetic intermediates in the preparation of a vast range of organophosphorus compounds,[1] but hitherto their structures in solution and bonding properties had not been extensively investigated.[2-5] In the past few years, investigations based upon lithiated amines[6-18] have shown similar structural and chemical properties to those observed for the lithiated organophosphorus compounds, as discussed in the following section.

The compounds formed by lithiation can be either ionically or covalently bonded in solution, and this has been found to be dependent upon the solvent.[6,19-23] Solvents of high polarity, for example tetrahydrofuran, lead to ionisation of the lithiated species, due to solvation of the lithium ion (Li^+) to form $Li^+(thf)_n$, resulting in the formation of an ionic monomeric species i.e.

$$"R_2PLi" \longrightarrow Li^+ + R_2P^-$$

which is observed as a sharp singlet resonance by phosphorus n.m.r. spectroscopy. Additionally, the lithiated diphosphine $PhPLi(CH_2)_2PLiPh$ prepared in THF, has been isolated in the crystalline form and is found to exist as $[Li_4(PhP(CH_2)_2PPh)_2(OC_4H_8)_8]$,[19] where each lithium atom is

associated with two molecules of THF. However, diethyl ether is found to be only weakly solvating, resulting in covalently bonded polymeric lithiated species i.e. ["RPLi"]$_n$, which are identified by the appearance of multiplet resonances from phosphorus n.m.r. spectroscopy.[21-24] Monomeric lithiated species formed in diethyl ether have been observed, which are covalently bonded and give rise to a 1:1:1:1 quartet as observed by phosphorus n.m.r. spectroscopy.[21]

The first reported examples of well resolved phosphorus-lithium couplings (in lithiated organophosphorus species) were measured in this Department.[24] From the analysis of the multi-element n.m.r. spectroscopic results, a Multicentre Electron Deficient Bonding Scheme (MEDB) was proposed as a possible bonding mechanism[23] in these lithiated species; indicative of covalent bonding in the observed monomeric, dimeric and trimeric species.

The aim of the current study was to extend the investigation into lithiated tricoordinated organophosphorus compounds principally: (i) to measure the hitherto unknown $^2J(^7Li-^1H)$ coupling constant, utilising multiple resonance experiments to determine their signs; and (ii) to confirm the basis used for analysis of the n.m.r. spectra and hence validate the proposed structures.

The following chapter discusses the routes taken to accomplish both (i) and (ii). These involved the preparation of selected primary and secondary phosphines, which were subsequently lithiated and studied by ^{31}P (I=1/2, natural abundance 100%), ^{13}C (I=1/2, natural abundance 1.1%), ^7Li (I=3/2, natural abundance 92.6%) and ^6Li (I=1, natural

abundance 7.4%) n.m.r. spectroscopy.

Disecondary diphosphines, $Ph(H)P(CH_2)_{\underline{n}}P(H)Ph$ where $\underline{n}$ = 2,3,4 or 6, were also prepared and lithiated in order to determine their structures in solution. The shorter chained diphosphine where $\underline{n}$ = 2 is now emerging as an important starting material in the synthesis of some interesting polyorganophosphorus compounds, which are described in Chapter 2.

One of the most widely used routes to lithiation of organophosphorus compounds is in the preparation of metal phosphides in THF[1], as shown below. However, this preparative method generates a mixture of lithiated species

$$R_3P + 2Li \xrightarrow{THF} R_2PLi + RLi$$

$$\text{e.g. } Ph_3P + 2Li \xrightarrow{THF} Ph_2PLi + PhLi$$

which are ionic due to the presence of THF.

Lithiations conducted in THF solutions are found by ^{31}P n.m.r. spectroscopy to give singlet resonances. This results from the high polarity of THF which leads to ionisation of the lithiated species, with THF association.

In one particular experiment a sample of lithiated diphenylphosphine in diethyl ether was observed by ^{31}P n.m.r. spectroscopy as a 'septet', indicating a lithiated dimeric species (Fig. 4.4). THF was added to this sample, and the phosphorus spectrum was then observed as a singlet, indicating ionisation of the lithiated dimeric species.

Thus, all experiments in this study were conducted

in diethyl ether, where no serious ionisation occurs.

The general preparative route used was as shown below. A variety of primary and secondary phosphines were prepared and lithiated using butyl lithium in diethyl ether. R = alkyl or aryl groups:

(1).

$$RPH_2 + \text{n-BuLi} \xrightarrow{Et_2O} \text{"[RP(H)Li]"} + \text{n-BuH}$$

(2).

$$R_2PH + \text{n-BuLi} \xrightarrow{Et_2O} \text{"[}R_2PLi\text{]"} + \text{n-BuH}$$

(3).

$$Ph(H)P(CH_2)_n P(H)Ph + 2\text{n-BuLi} \xrightarrow{Et_2O} \text{"[Ph(Li)P(CH}_2)_n\text{P(Li)Ph]"} + 2\text{n-BuH}$$

BONDING MECHANISM.

A wide range of lithiated organophosphorus compounds have now been studied, particularly the tricoordinated primary and secondary phosphines.[21,23,24] In preliminary work three types of structures have so far been found to be associated with these lithiated species in diethyl ether solutions:-

(a) a unique monomeric structure for $[(3,5\text{-}(Me)_3C)_2\text{-}C_6H_3(Me_3C)_4Li]$;[21]

(b) a large class of dimeric species e.g. $[Ph_2PLi]_2$;[24]

(c) a cyclic trimer in the case of $[Ph(H)PLi]_3$.[23]

From the analysis of the ^{31}P, ^{7}Li and ^{6}Li n.m.r. spectra of a variety of such species, two possible bonding mechanisms were proposed to account for the type of phosphorus-lithium associations observed: they were the phosphido-bridge and the multicentre electron bond deficient schemes.[23] The MEDB scheme was found to be the most reasonable when the two schemes are analysed with respect to phosphorus-lithium bonding and the data derived from the n.m.r. spectra.

The phosphido-bridge bonding scheme involves the phosphorus atom donating the lone pair of electrons to the lithium atom, thus forming a bridge between the two lithium atoms in, for example, the dimeric species (Fig. 4.1).

This scheme results in the tricoordinated phosphorus atom of the phosphine becoming tetracoordinated, leading

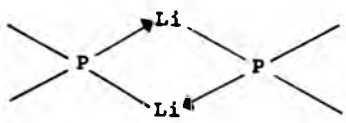


Fig. 4.1 : Schematic representation of phosphido-bridge bonding, for a dimeric lithiated organophosphorus species.

to a change in the molecular geometry: from a trigonal pyramidal geometry where predominantly p^3 orbitals are used to form σ-bonds, to a tetrahedral structure with sp^3 hybridised σ-bonds.

The phosphorus chemical shift values obtained for the lithiated species differed only slightly from those for the corresponding free phosphine, and the values of $^{1}J(P-H)$ for example in $[Ph(H)PLi]_3$= 180Hz, were found to be typical for tricoordinated phosphorus atoms.[23] These results indicated that the phosphorus atom had remained tricoordinated when associated with the lithium atoms. Additionally, it was found that the large values of $^{2}J(P-P)$ coupling constant measured for the lithiated species were typical of tricoordinated phosphorus atoms.[23] Table 4.1. compares the phosphorus chemical shifts of selected tricoordinated and tetracoordinated organophosphorus compounds. Table 2.2. shows the phosphorus chemical shifts obtained for a range of lithiated species, comparing them with the corresponding values of the related free phosphines. By this analysis, the MEDB scheme was favoured in which the phosphorus remains tricoordinated, retaining its lone pair of electrons.

The MEDB scheme involves the formation of a three-centre (3c), two electron (2e) bond, by the bridging of three atoms. Such bonding is typical of alkyllithium compounds, which are generally found to associate through triply bridging hydrocarbyl groups, using four-centre Li C bonds as found in the tetramer, $[MeLi]_4$.[20,25-29]

In the tetramer, four lithium atoms are situated at the corners of a regular tetrahedron, with each carbon atom localised over the centres of the four tetrahedral faces, forming a distorted cubic skeleton. Within this skeleton, the metal-carbon bonding is formed by four

Table 4.1. : ^{31}P chemical shift values for a range of tri- and tetra-coordinated organophosphorus compounds.

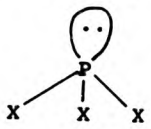
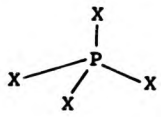
CHEMICAL SHIFT , δ , ppm. [1]	
TRICOORDINATED	TETRACOORDINATED
σ - BONDING, $(s)p^3$  TRIGONAL PYRAMIDAL	σ - BONDING, sp^3 hybridised  TETRAHEDRAL
PHOSPHINES	PHOSPHONIUM SALTS, R_4P^+
$MePH_2$ -163.5	$Ph_2P^+(Me)pentyl I^-$ +19.6
Me_2PH -98.5	$PhP^+(Me)(pentyl)_2\ I^-$ +21.8
$PhPH_2$ -122.0	$Me_4P^+I^-$ +25.1
Ph_2PH -41.0	$t\text{-}Bu_4P^+I^-$ +56.1
Ph_3P -8.0	PHOSPHORYL COMPOUNDS
PhMePH -71.0	$ClCH_2P(O)Cl_2$ +39.8
PHOSPHIDES	$Cl(CH_2)_2P(O)Cl_2$ +41.0
$KPMe_2$ -117.5	$C_6H_{13}P(O)Cl_3$ +62.0
$NaPPh_2$ -22.5	$PhP(O)Cl_2$ +34.5
NaPPhH -120.0	

Table 4.2. : ^{31}P chemical shift values for lithiated organophosphorus species and their corresponding free phosphine.

CHEMICAL SHIFT, δ, ppm.			
LITHIATED SPECIES		PHOSPHINE	
$[Ph_2PLi]$	-36.0	Ph_2PH	-40.5
$[PhMePLi]_2$	-91.0	PhMePH	-72.3
$[PhPHLi]_2$	-112.5	$PhPH_2$	-122.0
$[Et_3CPHLi]$	-105.9	Et_3CPH	-111.6
$[Me_3CPHLi]$	-73.9	Me_3CPH_2	-81.2

localised four-centre Li_3C bonds, with one over each face of the Li_4 tetrahedron (Fig. 4.2).

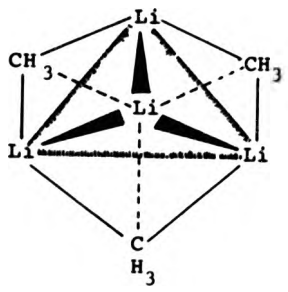


Fig. 4.2. : Schematic representation of the tetramer $[MeLi]_4$, where one methyl group directly behind the central lithium atom has been omitted.

Each carbon atom contributes an $\underline{sp}^3$ hybridised atomic orbital which overlaps with the three $\underline{sp}^3$ hybridised atomic orbitals supplied by the lithium atoms. All four hybridised orbitals point towards the centre of the Li_3C trigonal pyramid. The Li—C—Li bridging is thus accompanied by a three centre-two electron bond.

Similarly, in the formation of organophosphorus lithium compounds, the lithium atoms again may be regarded as $\underline{sp}^3$ hybridised and the role of the carbon atoms is assumed by the phosphorus atoms, leading to three centred -two electron bridge formation i.e. Li—P—Li. In this situation, the lone pair of electrons would be retained by the phosphorus atoms, thereby maintaining essentially the same geometry (Fig. 4.3).

Investigation of the lithiated organophosphorus species by ^{31}P n.m.r. spectroscopy reveals $^1J(P-^7Li)$ values of 37Hz. to 60Hz., indicating that both the

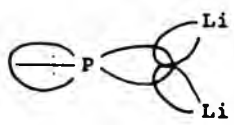


Fig. 4.3. : Schematic representation of a three-centred two electron bridge formation for a lithiated species.

phosphorus and lithium atoms are covalently bonded.[23] Additionally, the phosphorus chemical shifts indicate

tricoordination, thus demonstrating the applicability of the MEDB scheme.

The lithium alkyls have been extensively studied by ^{7}Li n.m.r. spectroscopy. The lithium atoms (ions) undergo rapid exchange reactions in solution at room temperature, with only singlet resonances being observed, thus resolved spectra are obtained at low temperatures. An important application of ^{7}Li n.m.r. spectroscopy was in the determination of the structure of $[MeLi]_4$ (sotopically enriched Carbon-13 samples were studied at low temperatures. Observed $^{1}J(^{13}C-^{7}Li)$ coupling constants of 15Hz provided important experimental evidence for the covalent nature of the alkyl-lithium bonding.[26]

^{31}P, ^{7}Li AND ^{6}Li N.M.R. SPECTRAL ANALYSIS OF LITHIATED PRIMARY AND SECONDARY PHOSPHINES.

The ^{31}P, ^{7}Li and ^{6}Li n.m.r. spectra obtained at room temperature for all the lithiated species prepared in this study, are observed either as a singlet, or as a broad resonance. At room temperature, the absence of any multiplet splittings is attributed to the rapid intermolecular exchange of the lithium atoms (ions), thus any interaction between phosphorus and lithium atoms is not observed.

At lower temperatures (below 235K) where multiplet structures are observed in some cases, the rate of intermolecular exchange decreases, enabling phosphorus-lithium coupling to be observed by ^{31}P, ^{7}Li and ^{6}Li n.m.r. spectroscopy.

It has been noted that an 'optimum temperature' is reached when well resolved multiplet structures are observed. However, some lithiated species are observed only as broad resonances even at low temperatures, although the measured resonance width (>200Hz), does indicate phosphorus-lithium coupling. The formation of polymeric species could possibly account for the non-resolution of multiplets in such cases. Additionally, loss of phosphorus-lithium coupling for some samples (below 200K (-73° C)) resulted from sample freezing, which is probably due to the lithiated species freezing as opposed to the solvent diethyl ether, which has a freezing point of 157K (-116° C).

Comparison of the phosphorus chemical shifts for the lithiated species with those for the free phosphine (Table

4.2.), shows a shift to low frequency, whereas for those species where the phosphorus atom retains a proton (i.e. lithiated primary phosphines) such shifts are in the high frequency direction. The low frequency shift implies additional shielding of the phosphorus (III) atom, which may be due to the delocalisation of electrons in the 3c-2e bonding system.

THE ANALYSIS OF OF MULTIPLET SPLITTINGS OF LITHIATED PRIMARY AND SECONDARY PHOSPHINES, AS OBSERVED BY ^{31}P, ^{7}Li, AND ^{6}Li N.M.R. SPECTROSCOPY.

The multiplet splittings arising from the phosphorus-lithium coupling and the magnitude of $^{1}J(P-^{7}Li)$ coupling constant of the lithiated species, gives an indication of the degree of association between the phosphorus and lithium nuclei; and hence the structure.

The following section describes the types of multiplet splittings observed with respect to the proposed structures of the lithiated species. Four types of structures have been shown to be associated with the prepared lithiated species; these are monomeric, dimeric, trimeric and tetrameric.

(A). DIMERIC SPECIES.

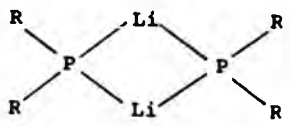


Fig. 4.4. : Diagrammatic representation of a dimeric species, where R = alkyl and/or aryl groups.

The ^{31}P n.m.r. spectrum of a dimeric species would be expected to show a symmetrical 1:2:3:4:3:2:1 septet (Fig. 4.5 and Spectrum 4.1.), indicating a first-order splitting.

The natural abundances of ^{7}Li atoms is 92.6% and of ^{6}Li atoms is 7.4%. In a dimeric system, where two lithium atoms are present, the respective probabilities of ^{7}Li and/or ^{6}Li atoms being present can be calculated:

$$\text{Two } ^{7}\text{Li atoms} = \left(\frac{92.6}{100}\right)^2 = 85.75\%$$

$$\text{Two } ^{6}\text{Li atoms} = \left(\frac{7.4}{100}\right)^2 = 0.55\%$$

$$\text{One } ^{7}\text{Li and one } ^{6}\text{Li atom} = 2\left[\left(\frac{92.6}{100}\right)\cdot\left(\frac{7.4}{100}\right)\right] = 13.70\%$$

These calculations indicate that the septet observed by ^{31}P n.m.r. spectroscopy and also predicted by the $(2nI+1)$ rule, arise from coupling to the statistically most probable combination of two ^{7}Li atoms. For ^{6}Li, $I = 1$;

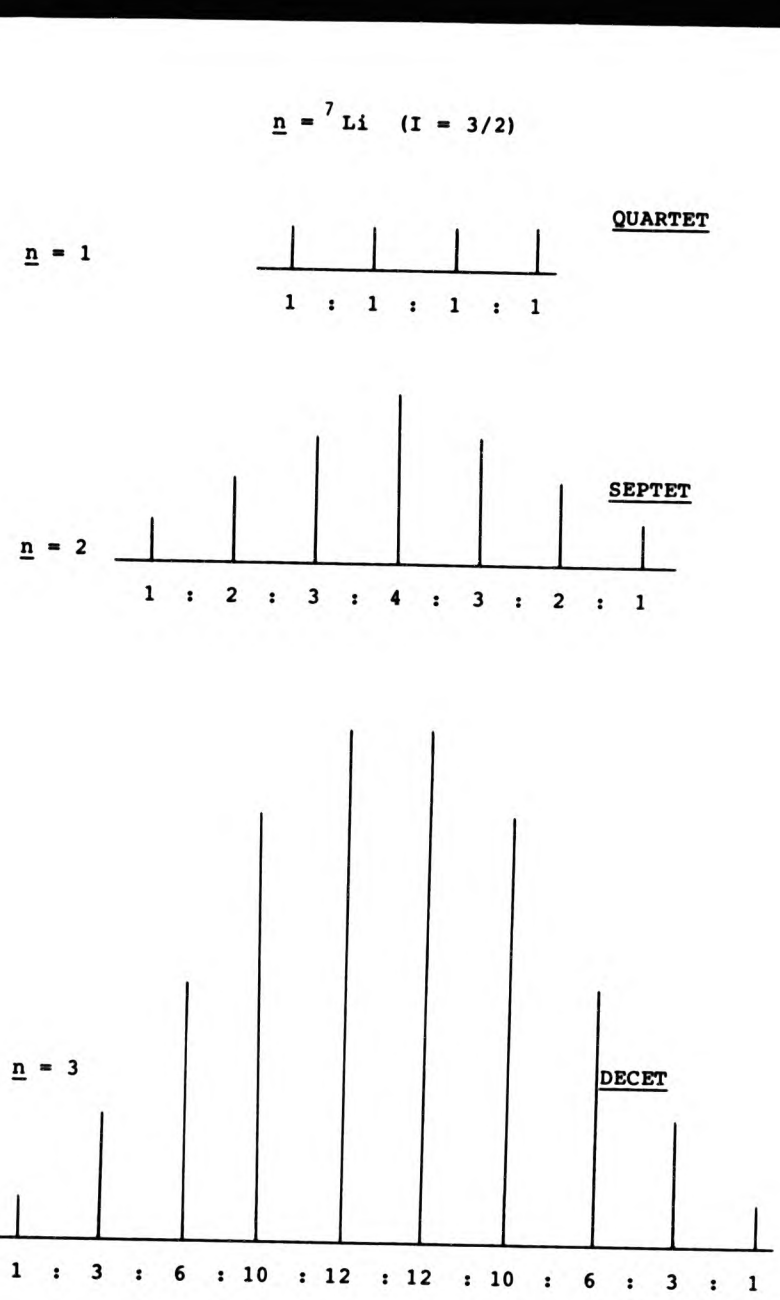
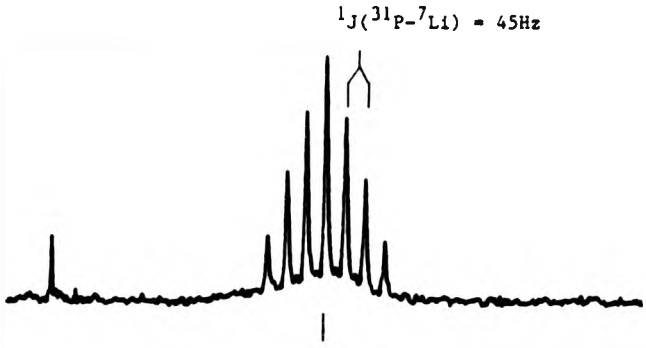


Fig. 4.5. : Schematic representation of the predicted multiplet structures, where I = 3/2.

Spectrum 4.1. : ^{31}P n.m.r. spectrum of $[Ph_2PLi]_2$ showing a symmetrical 1:2:3:4:3:2:1 septet, indicating a first-order splitting, in a dimeric species. Recorded at 190K.



if two such nuclei were present in the dimer, the ^{31}P n.m.r. spectrum would be resolved to show, by first-order splitting, a symmetrical 1:2:3:2:1 quintet. However, the previous probability calculations indicate that, the likelihood of encountering two ^{6}Li nuclei in the same lithiated species is negligble.

The relative intensities of the resonances in the multiplets, are determined by the number of ways in which n nuclei can be distributed amongst the possible energy states, which for ^{7}Li are -3/2, -1/2, +1/2, +3/2.

The ^{7}Li and ^{6}Li n.m.r. spectra are resolved as symmetrical 1:2:1 triplets, indicating a first-order splitting (Spectrum 4.2.), where two phosphorus nuclei are symmetrically associated with each lithium nucleus. The phosphorus n.m.r. data, of those lithiated species which exhibit the characteristic multiplet splittings predicted for symmetrical dimeric species, are shown in Table 4.3.

It is most important to note that the multiplet splittings predicted for dimeric species could also be produced by other symmetrical cyclic polymeric species, such as those shown in Figure 4.6. In such cases the number of phosphorus and lithium atoms directly bonded to each other is the same as in the dimeric species, and it is not possible to use the lithium or phosphorus spectra to distinguish them. However, by consideration of the ^{13}C n.m.r. spectrum, it is possible to unequivocally demonstrate that dimers are present. This depends upon the value of $^{1}J(P-P)$ being large and resulting in special types of second order spectra.

Spectrum 4.2 : ^{7}Li and ^{6}Li n.m.r. spectra of $[Ph_2PLi]_2$ showing a symmetrical triplet, indicating that two equivalent phosphorus atoms are associated with each lithium atom, in this dimeric species. Spectra recored at 190K.

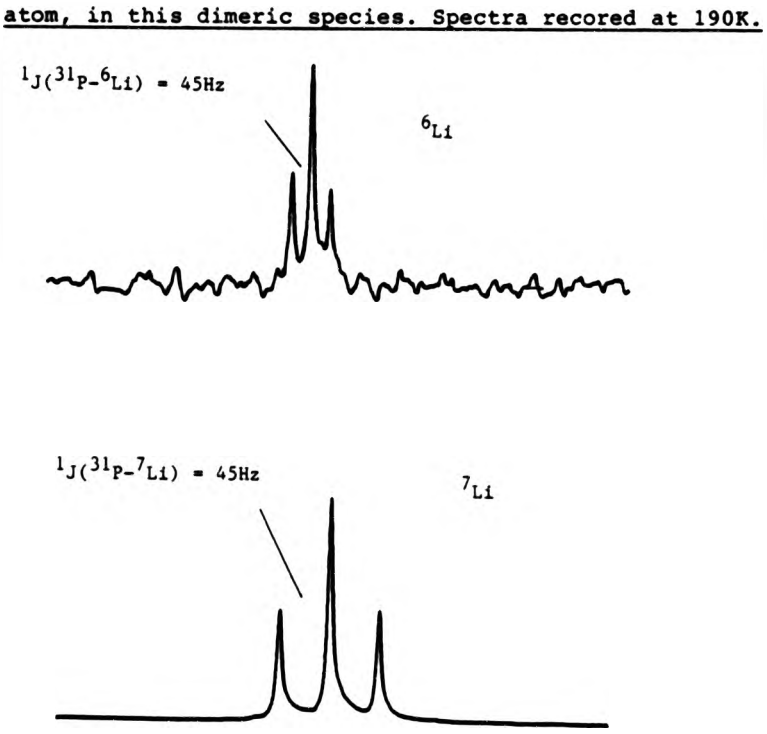


Table 4.3. : ^{31}P n.m.r. data for dimeric species.

DIMERIC SPECIES	TEMP (K)	CHEMICAL SHIFT		COUPLING CONSTANT
		PHOSPHINE	LITHIATED SPECIES	
		$\delta(^{31}P)$ ppm	$\delta(^{31}P)$ ppm	$^{1}J(^{31}P-^{7}Li)$ Hz
$[Ph_2PLi]_2$	190	-40.5	-38.5	45.0
$[n\text{-}Bu_2PLi]_2$	193	-69.6	-84.0	56.0
$[PhEtPLi]_2$	203	-52.8	-54.6	46.4
$[Phn\text{-}BuLi]_2$	203	-45.2	-62.6	46.4

NOTE.

(a). Chemical shifts relative to external 85% H_3PO_4.

(b). In Et_2O .

The ^{13}C n.m.r. spectrum of particular phenyl carbons for a dimeric species should arise from a second-order AA'X spin system; whilst a cyclic trimer should arise from an AA'_2 X spin system; a cyclic tetramer from an AA'_2 A''X spin system; and a cyclic pentamer from an AA'_2 A''_2 X spin system (see Fig. 4.6 for the labelling scheme).

For large ^{2}J(P -P), the X (i.e. ^{13}C) spectra of these different systems will be of markedly different appearance. (Spectrum 4.3.)

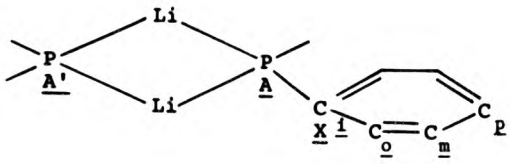
The X part of an AA'X spin system consists of five lines. If $^{2}J(P_{A}-P_{A'})$ is very large then only a triplet is observed. (See Appendix for a full description.)

Similarly, for large $^{2}J(P_{A}-P_{A'})$ the X part of an $AA'_{2}X$ spin system (e.g. from a cyclic trimer) would be a 1:3:3:1 quartet. Similar spectra, to those obtained for cyclic trimers would be predicted for cyclic tetramers and pentamers. It is assumed that long range coupling over five bonds, $^{5}J(P_{A'}-P_{X})$, is very small or zero.

Two experiments have been conducted to confirm unequivocally the presence of dimeric structures.

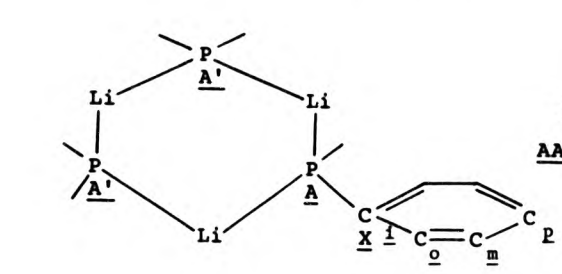
EXPERIMENT 1.

In principle any of the carbon-13 nuclei of the phenyl group in "Ph_2PLi" could be used to provide the required information, but for the experiment at low temperature to succeed, it is necessary that $J(P-^{13}C)$ should be resolvable. In practice, this meant that it was necessary to confine the attention to the ipso and ortho carbons. The former give a triplet (Spectrum 4.4.) thus showing
(a) that $^{2}J(P-P)$ must be large, and
(b) that the system is AA'X with N = 19.5Hz. That is, it arises from a dimeric structure. These results are confirmed by the appearance of the ortho carbons which give a less well resolved triplet with N = ca 13Hz. The line widths in the carbon n.m.r. spectrum are ca 5Hz and this prevented



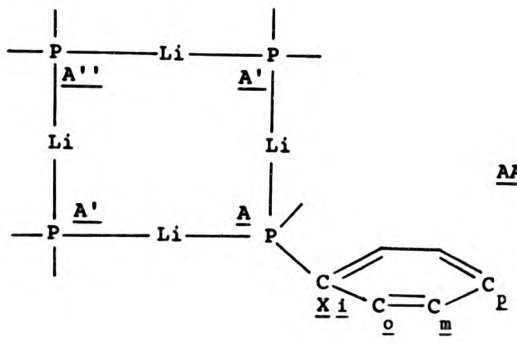
DIMER

AA'X SPIN SYSTEM.



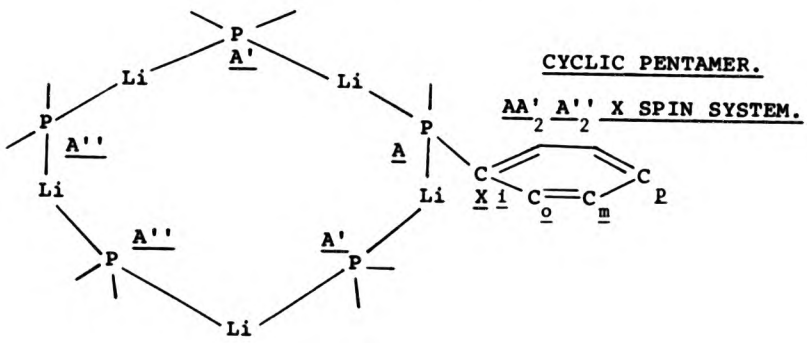
CYCLIC TRIMER

AA'_2 X SPIN SYSTEM.



CYCLIC TETRAMER.

$AA'_2A''X$ SPIN SYSTEM.

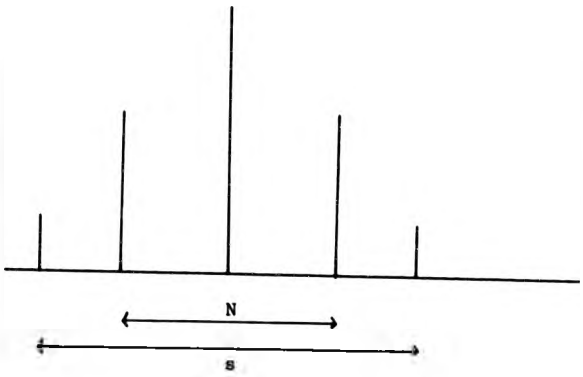


CYCLIC PENTAMER.

$AA'_2A''_2$ X SPIN SYSTEM.

Fig. 4.6. : Labelling scheme for a variety of lithiated species.

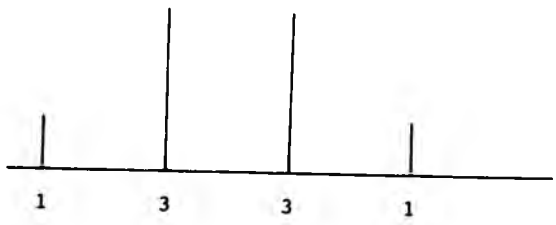
CYCLIC DIMER—AA'X SPIN SYSTEM



CYCLIC TRIMER—AA'_2X SPIN SYSTEM

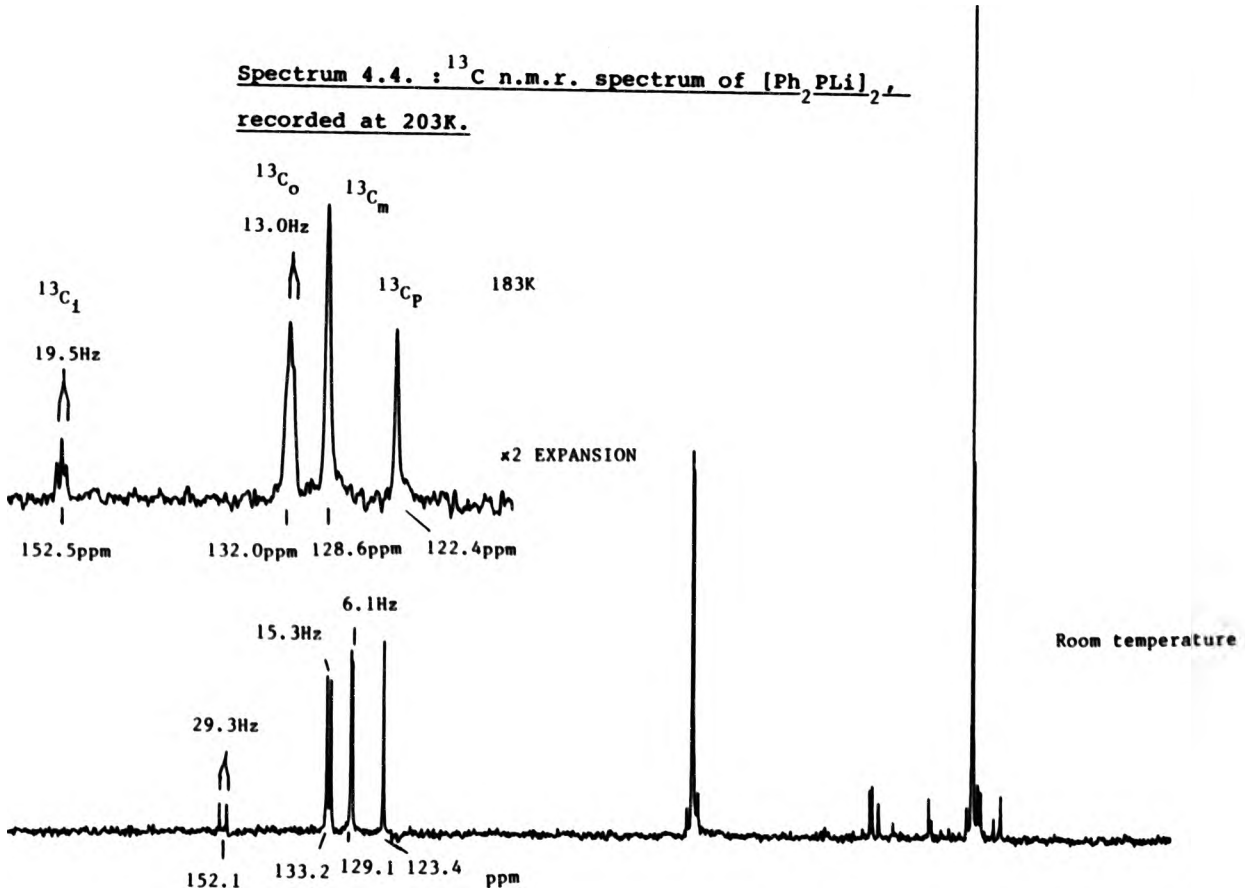
CYCLIC TETRAMER—$AA'_2A''X$ SPIN SYSTEM

CYCLIC PENTAMER—$AA'_2A''_2X$ SPIN SYSTEM



Spectrum 4.3. : Schematic representations of the X part (i.e. ^{13}C) of $AA'X$, AA'_2X, $AA'_2A''X$ and $AA'_2A''_2X$ spin systems where it is taken that J(P-P) is large.

Spectrum 4.4. : ^{13}C n.m.r. spectrum of $[Ph_2PLi]_2$, recorded at 203K.



the observation of any fine structure of the meta and para resonances.

This result from the ^{13}C n.m.r. spectrum shows that $^{2}J(P_A - P_{A'})$ is <u>large</u>, otherwise an AA'X spin system as predicted for dimeric species and proposed for $[Ph_2PLi]_2$ would not have been found. Additionally, if the $^{2}J(P_A - P_{A'})$ coupling constant had been <u>small</u>, the ^{13}C-P couplings would have appeared as doublets, for the dimeric and polymeric species. Thus, it would not then have been possible to unequivocally determine the structures of the lithiated species.

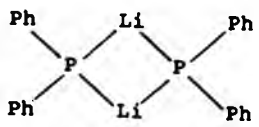
<u>EXPERIMENT 2.</u>

It was thought desirable to confirm the large magnitude of $^{2}J(P_A - P_{A'})$ independently. From these n.m.r. spectra, the magnitude of $^{2}J(P_A - P_{A'})$ could not be determined, nor can it be measured directly from the ^{31}P n.m.r. spectrum. Thus, an unsymmetrical lithiated species was formed by the addition of butyl-lithium in hexane to a solution containing diphenylphosphine and di-<u>n</u>-butylphosphine in diethyl ether. These two phosphines were chosen because:-

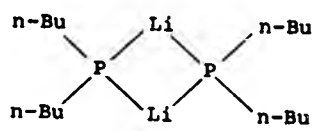
<u>(i).</u> The respective lithiated species of each were known to exist in the dimeric form;

<u>(ii).</u> There is a chemical shift difference of <u>ca</u> 50ppm between the two lithiated species.

(iii). It is to be expected that the following three species would be present as dimers in solution, probably in the expected ratios of 1:1:2, as shown below. If one



1



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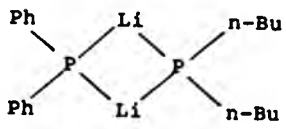
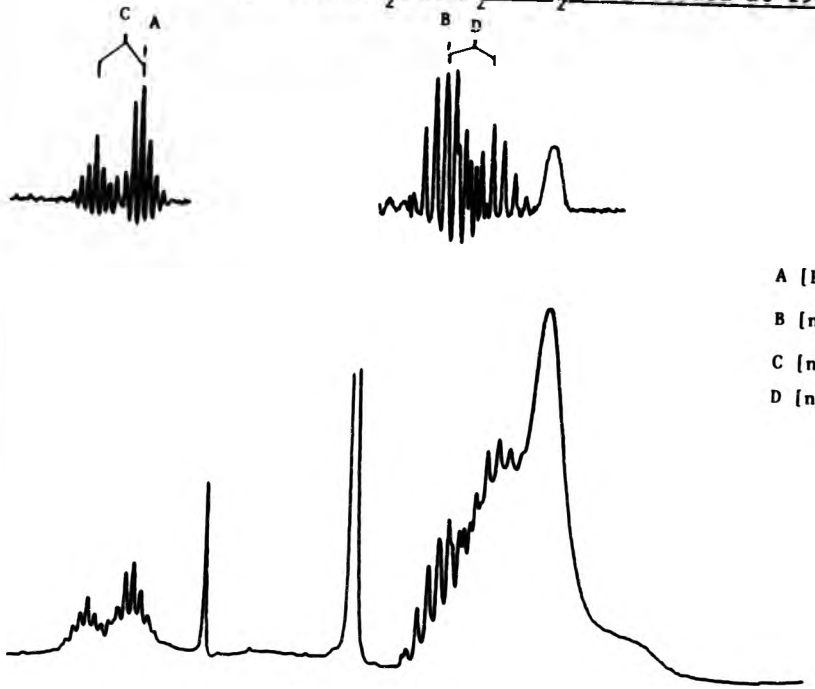


3

of the phosphines were used in excess e.g. a 1:5 ratio of Ph_2PH : $n\text{-}Bu_2PH$, then it would be expected that a substantial amount of the mixed lithiated species and the symmetrical dimer from $n\text{-}Bu_2PH$ would form as opposed to $[Ph_2PLi]$. Thus in the Ph region this would reduce the overlapping of the resonances from $[Ph_2PLi]$ and the mixed dimer, resulting in the intensity of the mixed dimer being stronger. The measured intensity is found to be in the ratio of 1:5 for $[Ph_2PLi]_2$: $[Ph_2PLi_2P(n\text{-}Bu)_2]$.

In the ^{31}P n.m.r. spectrum obtained at 190K four symmetrical septets for the mixed dimer can be observed (Spectrum 4.5.), where $^1J(P_{Ph_2} - {}^7Li) = 38.0Hz$, $^1J(P_{n\text{-}Bu_2} - {}^7Li) = 60.0Hz$, and $^2J(P_A - P_A) = 244.0Hz$. The results obtained are presented in Table 4.5. Additionally at $\delta(P) = -69.6ppm$ there is

Spectrum 4.5. : ^{31}P n.m.r. spectrum of the mixed lithiated species $[Ph_2P(Li)_2Pn\text{-}Bu_2]$. Recorded at 190K.



	$^1J(^{31}P\text{-}^7Li)$Hz	$^1J(^{31}P\text{-}^{31}P)$Hz
A $[Ph_2PLi]_2$	45	
B $[n\text{-}Bu_2PLi]_2$	59	
C $[n\text{-}Bu_2PLi_2P^*Ph_2]$	38	244
D $[n\text{-}Bu_2{}^*PLi_2PPh_2]$	60	244

an obscurred signal from the more abundant lithiated phosphine $[(n\text{-Bu})_2PLi]_2$.

The result from these experiments shows that $^2J(P_A-P_{A'})$ is very large and thus confirms the assumptions made in the analysis of the ^{13}C n.m.r. spectrum for the dimeric species. Hence, the lithiated species in Table 4.5. which reveal symmetrical septets (i.e. equal line spacings), and with an intensity pattern of 1:2:3:4:3:2:1 can be taken to be dimeric in structure.

TABLE 4.4.

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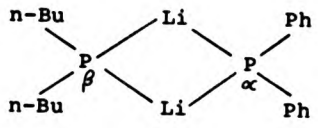
Table 4.5. : ^{31}P n.m.r. data obtained for the mixed lithiated species.



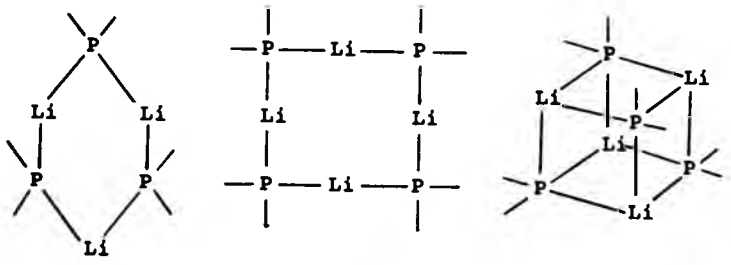
TEMP. (K)	CHEMICAL SHIFT, δ, ppm		COUPLING CONSTANT, J, Hz.	
	PHOSPHINE	LITHIATED SPECIES	$^{1}J(P-^{7}Li)$	$^{2}J(P_A-P_{A'})$
190	Ph_2PH = -40.5	α = -38.0	60.0	244.0
	$n\text{-}Bu_2PH$ = -69.6	β = -90.0	38.0	

NOTE

(a). Chemical shifts relative to external 85% H_3PO_4.

(b). In Et_2O.

(B). TRIMERIC AND TETRAMERIC SPECIES.



CYCLIC TRIMER CYCLIC ---- TETRAMER ---- CUBIC

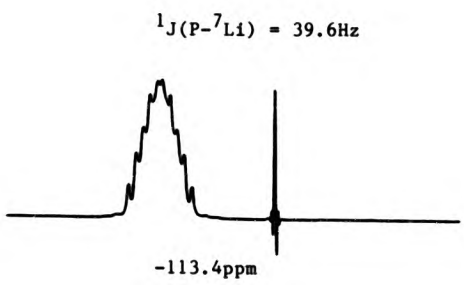
Fig. 4.7. : Schematic representation of trimeric and tetrameric lithiated species.

(a) CYCLIC TRIMERS.

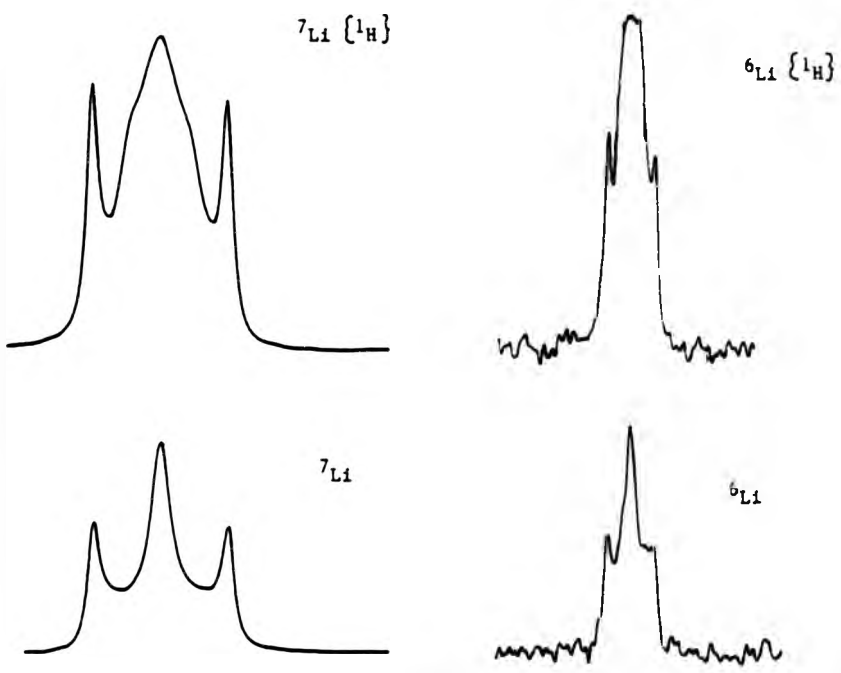
The only observed cyclic trimer is $[PhHPLi]_3$;[23] this species was prepared and its ^{31}P n.m.r. spectrum was observed as a decet with uneven line spacing, (Fig. 4.7 and Spectrum 4.6.). The ^{31}P proton-coupled n.m.r. spectrum indicated further coupling by the proton bonded to the phosphorus, where $^{1}J(P-{}^{1}H) = 180Hz$. (Spectrum 4.6.).

Spectrum 4.7 shows ^{7}Li and ^{6}Li spectra with and without proton decoupling. The changed appearance however is not due to the removal of a Li-H coupling interaction because the outer ("N") lines remain sharp throughout. Rather, it arises from a difference in the degree of second

Spectrum 4.6. : ^{31}P n.m.r. spectrum of the trimer $[PhHPLi]_3$ showing an unsymmetrical decet, recorded at 200K.



Spectrum 4.7. : ^{7}Li and ^{6}Li n.m.r. spectra of $[PhHPLi]_3$ trimer, showing second order effects indicating coupling of ^{7}Li nuclei to inequivalent ^{31}P nuclei. Recorded at 200K.

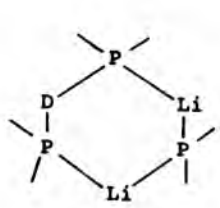


order character of the ^{31}P spectrum brought about by the absence or presence of the large P-^{1}H spin coupling interaction. That is, in the presence of proton decoupling the spin system is AA'A''XX'X'' whereas in its absence it is AA'A''MM'M''XX'X''.

The structure of this species was determined in two ways.[30] Firstly, the two outermost sharp lines observed in the ^{7}Li n.m.r. spectrum, in either the presence or absence of proton decoupling, will arise from molecules where all the phosphorus nuclei are in the same spin state (i.e. all +1/2 or -1/2). The remaining lines arise from molecules in which the phosphorus nuclei are not all in the same spin state; the lines occupy positions which are dependent upon the various (^{31}P- ^{7}Li), (^{31}P- ^{31}P) and (^{7}Li- ^{7}Li) couplings. However, using Pascal's rule for multiplicity and the line intensity for nuclei with spin I = 1/2, the ratio of the line intensity of the pair of outer lines, with respect to the intensities of the remaining lines, can be calculated as 1:1 for a dimer, 1:3 for a trimer, 1:7 for a tetramer and 1:31 for a hexamer; irrespective of the degree of second order character.

However, due to overlapping of lines, a precise measurement was not possible. An approximate measurement made for this species gave a ratio of 1:5, which indicated either a trimer or tetramer. Secondly, by computer simulation, spectra were derived for the three structures, shown in Figure 4.7. When matched to the actual spectra obtained, these indicated that, the species $[PhHPLi]_3$ was trimeric.

Using this species, an experiment was conducted to determine whether a proton bridging was possible in this cyclic trimeric system. The trimer was prepared using deuterated phenylphosphine ($PhPD_2$), to form $[PhD_n P\ Li_n]$ where n = 1, 2 or 3, as shown below.



The ^{31}P and ^{7}Li n.m.r. spectra obtained for the species, were identical to those obtained for the undeuterated lithiated species. The ^{2}D n.m.r. spectrum indicated the presence of $CH_3CH_2CH_2D$ (Equation 4.1.), as a sharp line; a broad signal underneath could not be resolved. Hence, it was not possible to confirm the

$$PhPD_2 + n\text{-BuLi} \xrightarrow{Et_2O} [PhDPLi]_3 + n\text{-BuD}.$$

EQUATION 4.1.

presence of bridging deuterium in the lithiated cyclic system. However, in a similar experiment, using $n\text{-Bu}_2PD$ (see Experimental chapter), it was found that a deuterium atom was not part of this dimeric species (Equation 4.2.); thus assuming analogous behaviour, it may follow that a deuterium atom is not present in the cyclic trimeric system.

$$n\text{-Bu}_2PD + n\text{-BuLi} \xrightarrow{Et_2O} \text{"}[n\text{-Bu}_2P]_2LiD\text{"} + n\text{-BuD}$$

EQUATION 4.2.

(b). TETRAMERIC SPECIES.

CUBIC TETRAMER.

The ^{31}P n.m.r. spectrum for the cubic tetramer (Fig. 4.7.), would be predicted as a symmetrical 1:3:6:10:12:12:10:6:3:1 decet; indicating that three lithium atoms are symmetrically associated with one phosphorus atom, and that $^{3}J(P-^{7}Li)$ is small or zero. The ^{7}Li n.m.r. spectrum would be expected to consist of a symmetrical 1:3:3:1 quartet, indicating that three phosphorus atoms are symmetrically associated with one lithium atom, again assuming that $^{3}J(P-^{7}Li)$ is small or zero.

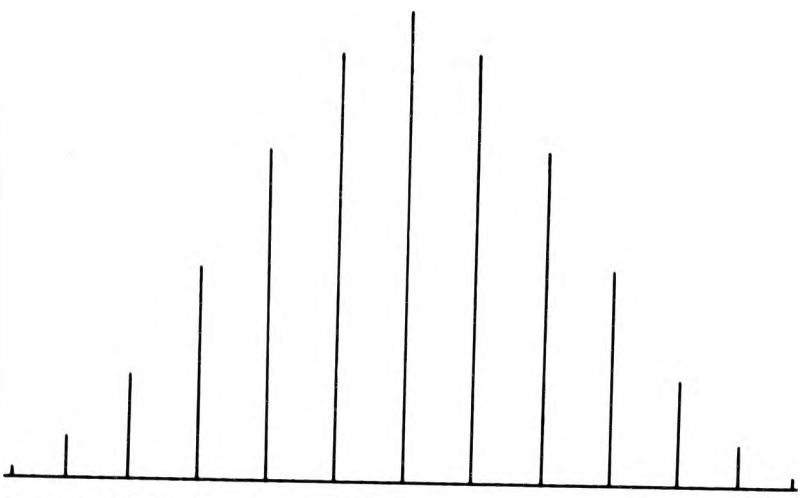
The ^{31}P n.m.r. spectrum of the lithiated species "$[(i\text{-}Pr)_2PLi]$", is observed as a symmetrical multiplet, of which only eight lines are observed (Spectrum 4.8.). Thus, one can speculate that the fully resolved multiplet could either be a decet where $\underline{n} = 3$ (^{7}Li), or a thirteen line multiplet where $\underline{n} = 4$. In order to obtain an eight line multiplet, $\underline{n}$ must be 2.5 which is unrealistic! Figure 4.8 is a schematic representation of two P n.m.r. spectra where $\underline{n} = 3$ and $\underline{n} = 4$. From the intensities of the resonances obtained for "$[(i\text{-}Pr)_2PLi]$", the multiplet is found to most closely resemble the spectrum where $\underline{n} = 3$, with the two central lines being of equal intensity. This is not the case where $\underline{n} = 4$.

The ^{7}Li and ^{6}Li n.m.r. spectra could not be fully resolved (Spectrum 4.9.) in order to determine conclusively the number of phosphorus nuclei associated with each

(A)

1 : 3 : 6 : 10 : 12 : 12 : 10 : 6 : 3 : 1

(B)

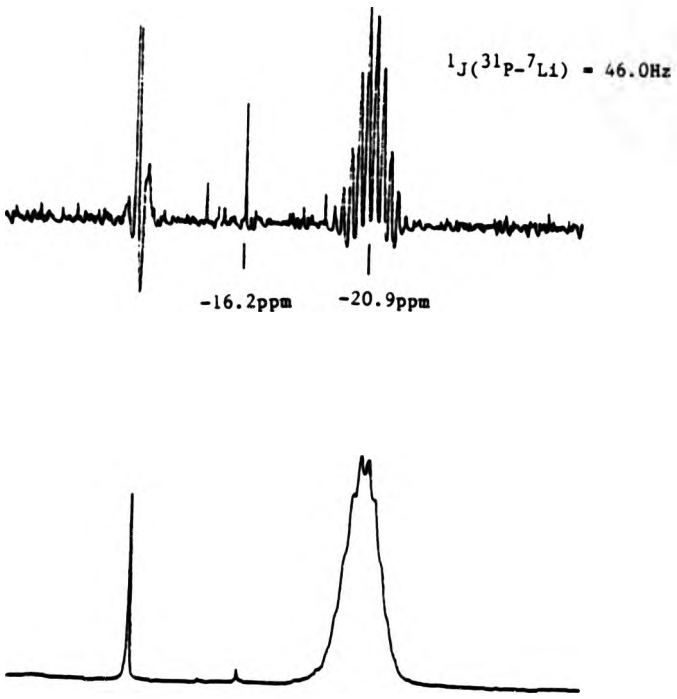


1 : 4 : 10 : 20 : 31 : 40 : 44 : 40 : 31 : 20 : 10 : 4 : 1

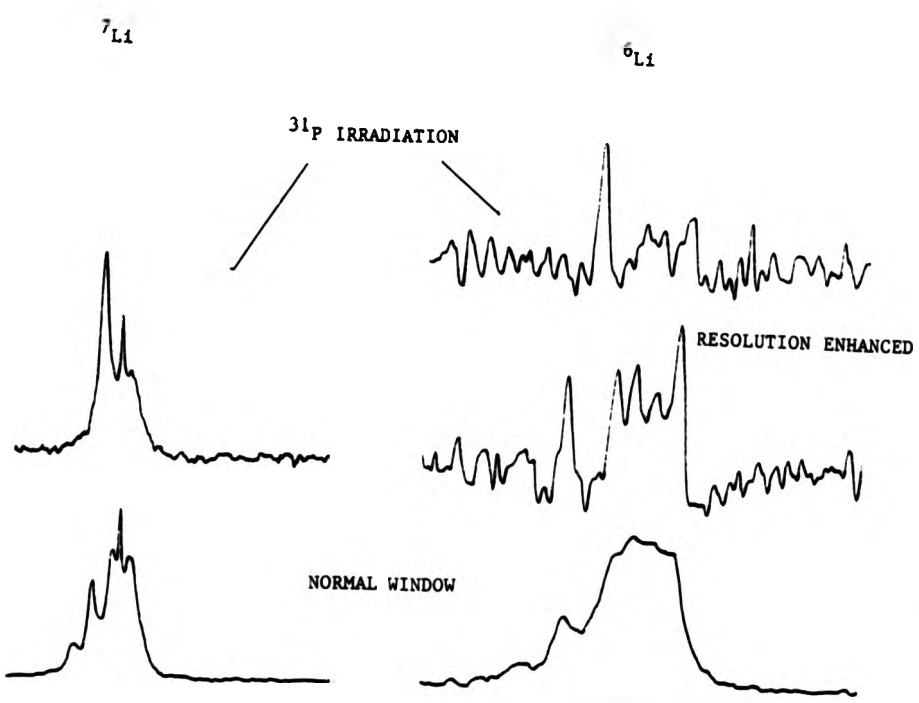
Fig. 4.8. : Schematic representation of ^{31}P n.m.r. spectra when (A) n = 3 and (B) n = 4, where $^{1}J(P-{}^{7}Li)$ are the same for each set of multiplets, but can differ between various lithiated species.

Spectrum 4.8. : ^{31}P n.m.r. spectrum of "[(i-Pr) PLi]", showing a symmetrical decet. Recorded at 200K.

RESOLUTION ENHANCED SPECTRUM



Spectrum 4.9. : ^{7}Li and ^{6}Li n.m.r. spectra of "[(i-Pr)$_2$PLi]"$_4$. Recorded at 200K.



lithium nucleus. However, it is tentatively suggested that "$[(i\text{-}Pr)_2PLi]_4$" exists as a cubic tetramer.

As yet a monocyclic tetramer has not been identified in this study.

(C). MONOMERIC SPECIES.

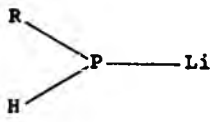


Fig. 4.9. : Diagrammatic representation of a monomeric species.

The ^{31}P n.m.r. spectrum of a monomeric species would be expected to consist of a symmetrical 1:1:1:1 quartet, indicating that one lithium atom is associated with one phosphorus atom. The ^{7}Li n.m.r. spectrum would be expected to consist of a 1:1 doublet, indicating that one phosphorus atom is associated with one lithium atom.

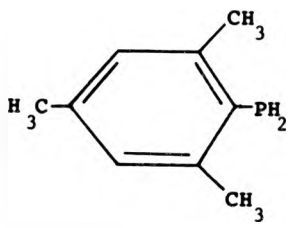
Attempts were made to prepare monomeric species possessing a protonated phosphorus atom, in order to measure the coupling $^{2}J(^{7}Li\text{-}^{1}H)$, and then to use multiple resonance experiments to determine signs of the coupling constants. The monomeric species was chosen for its potential structural simplicity and because it would enable direct measurement of the $^{2}J(^{7}Li\text{-}^{1}H)$ coupling constant; whilst avoiding complications due to additional long range coupling, which may occur in the larger lithiated structures.

For the preparation of a monomer, bulky primary phosphines were synthesised, as it had been noted that the size of the substituents bonded to the phosphorus atom, appeared to influence the type of lithiated species formed; in that the degree of association between phosphorus

and lithium atoms decreased as the substituents became bulkier. However, this does not hold true with respect to the lithiated species formed using 2,4,6-tri-methyl-phenylphosphine (Fig. 4.10). For this experiment two bulky primary phosphines were lithiated, see Figure 4.10.

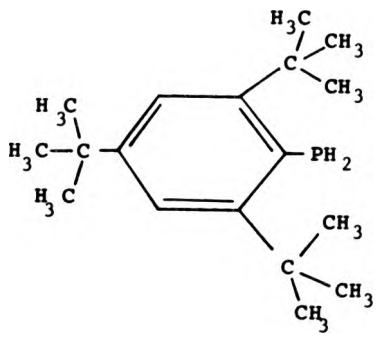
The ^{31}P proton-coupled n.m.r. spectra for both lithiated phosphines were observed as 1:1 doublets, where $^{1}J(P-^{1}H)$ = 190Hz, indicating that one proton remains directly attached to a phosphorus atom in each case.

The ^{31}P n.m.r. spectrum of lithiated (A) was found to consist of an unsymmetrical multiplet, possibly indicating the presence of species containing several lithium



(A)

2,4,6-TRIMETHYLPHENYLPHOSPHINE



(B)

2,4,6-TRI-TERT-BUTYLPHENYLPHOSPHINE

Fig. 4.10. : Structural representation of two bulky primary phosphines used to form monomeric species.

FIG 4·11.

PAGINATION
ERROR

atoms associated with each phosphorus atom. The ^{7}Li and ^{6}Li n.m.r. spectra could not be fully resolved to tentatively assign a structure to this species.

The ^{31}P n.m.r. spectrum of lithiated (B) seemed to indicate the presence of a monomer, but the multiplet lines could not be fully resolved. The signal observed as a broad flat topped structure, with $\nu_{\frac{1}{2}}$ = 190-200Hz, which indicates the presence of a multiplet. The ^{7}Li and ^{6}Li n.m.r. spectra were also unresolvable.

^{31}P, ^{7}Li AND ^{6}Li N.M.R. SPECTRAL ANALYSIS OF LITHIATED DISECONDARY DIPHOSPHINES.

PREPARATION.

The disecondary diphosphines lithiated are mppe, mppp, mppb and mpph (Fig. 4.13), with n = 2,3,4 and 6 respectively.

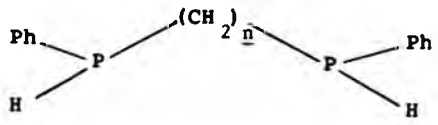


Fig. 4.13. : Structural representation of disecondary diphosphines, where n = 2,3,4 and 6.

Three samples were prepared for each diphosphine containing different molar ratios of n-BuLi in diethyl ether. (Table 4.6.).

Table 4.6.

SAMPLE	MOLAR RATIO		
	M. n-BuLi	:	DISECONDARY DIPHOSPHINE
(a)	0.5	:	1.0
(b)	1.0	:	1.0
(c)	2.0	:	1.0

(1). LITHIATED BIS-1,2-(MONOPHENYLPHOSPHINO)ETHANE, mppe.

SAMPLE (a) and (b).

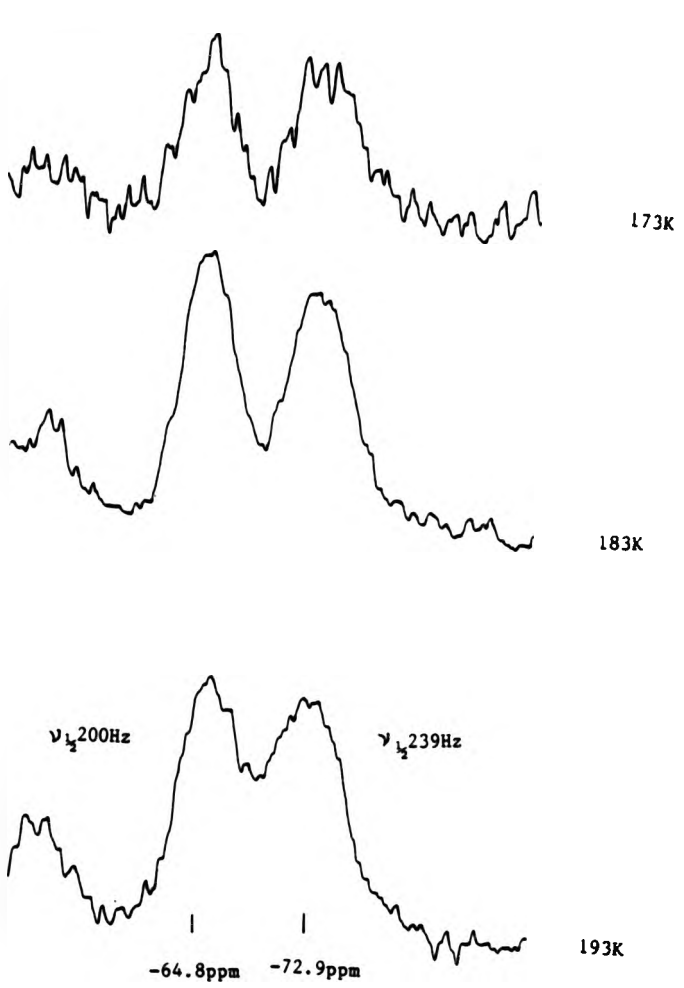
At room temperature, the ^{31}P n.m.r. spectrum indicates the presence of the two diastereoisomers of mppe as two sharp singlet resonances at δ(P) = -47.4ppm and -47.8ppm; and two broad signals at δ(P) = -69.2ppm (weak signal) and -72.6ppm (strong signal).

At 213K, the weak signal is no longer observed with the broad signal showing $\nu_{\frac{1}{2}}$ = 233Hz.

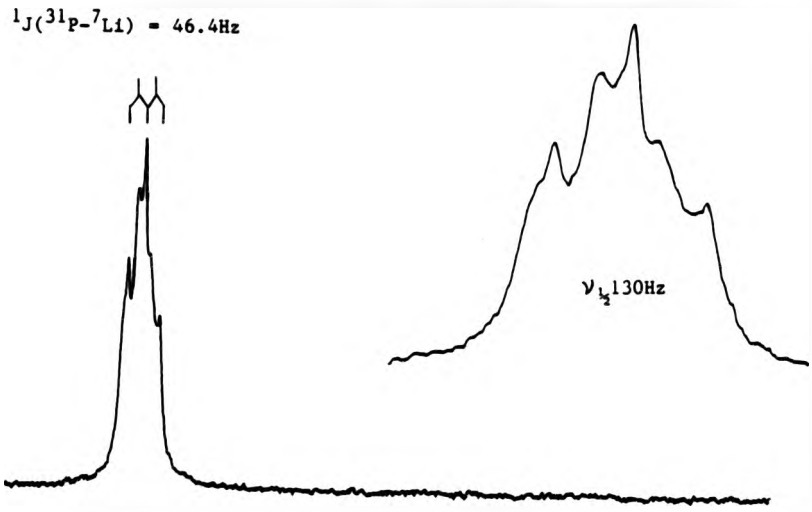
At 193K and 173K, the two broad signals are again observed at δ(P) = -64.9ppm and δ(P) = -72.9ppm, but now they are of approximately equal intensity, with $\nu_{\frac{1}{2}}$ = 200Hz and 239Hz respectively. (Spectrum 4.10.)

The ^{7}Li n.m.r. spectrum at 173K reveals the presence

Spectrum 4.10. : ^{31}P n.m.r. spectrum of lithiated mppe at 193K.



Spectrum 4.11. : ^{7}Li n.m.r. spectrum of lithiated mppe at 173K.



of a number of overlapping resonances, from which a possible triplet can be identified with $^{1}J(P-^{7}Li)$ = 46.4Hz.

SAMPLE (c).

The ^{31}P n.m.r. spectrum at 200K reveals two broad signals at $\delta(P)$ = -69.7ppm and $\delta(P)$ = -77.6ppm with $\nu_{\frac{1}{2}}$ = 600-700Hz. The ^{7}Li n.m.r. spectrum at 200K was observed as a broad signal.

It is not possible to conclusively define a structure from the results obtained for this system. The ^{7}Li n.m.r. results from samples (a) and (b) seem to indicate the possible presence of a dimeric species. However, from the ^{31}P n.m.r spectral results the two broad signals would seem to imply that a polymeric structure is present. Thus, it could be postulated that the dimer is incorporated within a polymeric system as shown in Figure 4.14, but there are other possibilities.

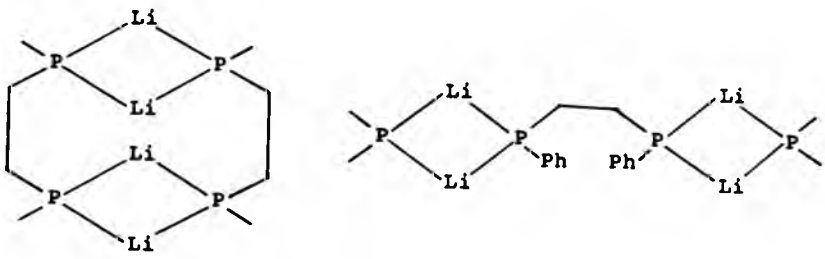


Fig. 4.14. : Schematic representation of two possible structures formed by the lithiated mppe species.

(2). LITHIATED BIS-1,3-(MONOPHENYLPHOSPHINO)PROPANE, mppp.

SAMPLE (a).

At room temperature, the ^{31}P n.m.r. spectrum indicates the presence of mppp as a sharp singlet at δ(P) = -54.6ppm, and there is also a broad signal at δ(P) = -83.5ppm.

At 233K, three singlets are observed at δ(P) = -51.9ppm, -53.6ppm and -53.8ppm; and three broad signals at δ(P) = -63.8ppm, -74.4ppm and -85.1ppm. From previous lithiation experiments broad signals have usually been indicative of unresolved multiplets, arising from lithiated species.

At 203K, a well resolved septet is observed at δ(P) = -62.6ppm, with $^{1}J(P-^{7}Li)$ = 47.6Hz, indicating that two lithium atoms are associated with one phosphorus atom. The ^{7}Li n.m.r. spectrum at this temperature shows a 1:2:1 triplet, with $^{1}J(P-^{7}Li)$ = 47.6Hz, indicating that two phosphorus atoms are associated with one lithium atom. (Spectra 4.12. and 4.13.). The other two broad signals previously observed are no longer seen. In addition the three singlet resonances were still observed and the proton-coupled ^{31}P n.m.r. spectrum revealed doublets centred at -51.0ppm and -53.5ppm, with respective couplings of $^{1}J(P-^{1}H)$ = 204Hz and 208Hz. Thus, the phosphorus atoms giving rise to these signals are directly bonded to a proton. The resonance at -51.0ppm is thought to be associated with the lithiated species; that at -53.5ppm is assigned to mppp. The singlet at -53.1ppm is thought to arise from

the diastereoisomer of mppp, and was unobservable at room temperature because the signals were only 0.4ppm apart.

The ^{31}P and ^{7}Li n.m.r. spectra possibly indicate the presence of a dimeric structure similar to that shown in Figure 4.12.

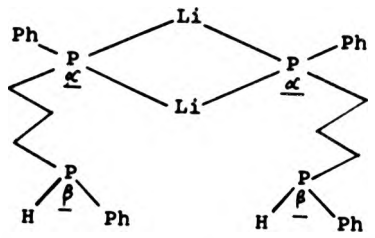
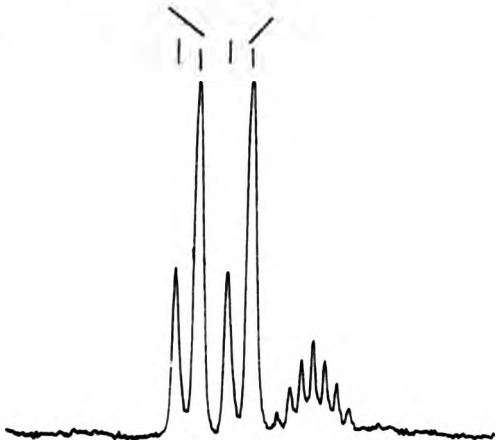


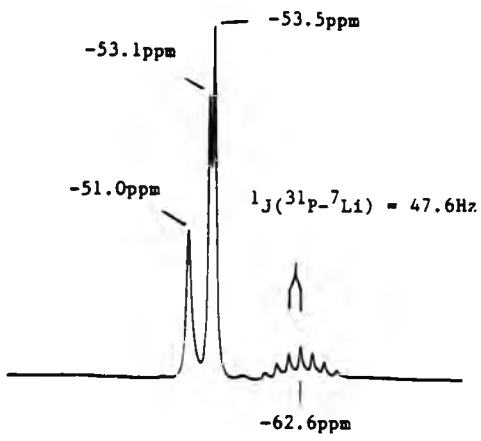
Fig. 4.12. : Diagrammatic representation of the possible structure of the lithiated species present in sample (a).

This structure possesses two pairs of inequivalent phosphorus atoms $^{31}P_{\alpha}$ and $^{31}P_{\beta}$. The $^{31}P_{\alpha}$ atoms associated with lithium atoms give rise to the septet at $\delta(P)$ = -62.6ppm, with $^{1}J(P_{\alpha}-{}^{7}Li)$ = 47.6Hz. Whilst the $^{31}P_{\beta}$ atoms, retaining a proton, are observed as a singlet at $\delta(P)$ = -51.0ppm. Long range couplings $^{4}J(P_{\alpha}-P_{\beta})$ and $^{5}J(P_{\beta}-{}^{7}Li)$ are not observed and are taken to be zero.

Spectrum 4.12. : ^{31}P proton-coupled and decoupled n.m.r. spectra of lithiated mppp sample (a), recorded at 203K.

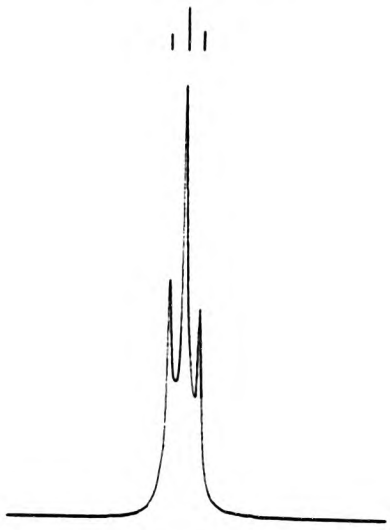
$^{1}J(^{31}P-^{1}H)$ = 204.0Hz $^{1}J(^{31}P-^{1}H)$ = 208.7Hz





Spectrum 4.13. : ^{7}Li n.m.r. spectrum of mppp sample (a), recorded at 203K.

$^{1}J(^{31}P-^{7}Li) = 47.6Hz$



SAMPLE (b).

The ^{31}P n.m.r. spectra obtained at room temperature and various low temperatures, to 183K, show the same resonances as observed for sample (a). However, closer inspection of the septet at 193K, reveals a weaker underlying septet, with $^{1}J(P-^{7}Li)$ = 47.6Hz (Spectrum 4.14.). The ^{7}Li n.m.r. spectrum shows a 1:2:1 triplet. The position of the second septet would seem to indicate a close molecular relationship to the primary septet. There are two possible explanations for the second septet:

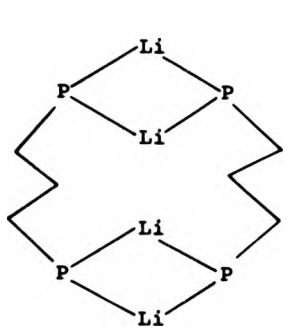
(1). The septet may arise from the lithiation of the second diastereoisomer of mppp, forming a structure similar to that shown in Figure 4.14. The two forms then differ in the orientation of the lone pair of electrons of the two lithiated $^{31}P_{\alpha}$ atoms. However, in this case a resonance from the $^{31}P_{\beta}$ atoms would be expected close to that observed for $^{31}P_{\beta}$ at -51.0ppm, but this is not observed.

(2). If lithiation occurs in a step-wise fashion, then it could be that the initial species (Fig. 4.12), is further lithiated, as shown in Figure 4.13. (Using molecular models, the ring structure seems feasible.).

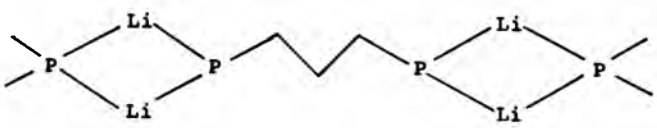
Additionally, at 193K and 183K, the broad signal at $\delta(P)$ = -71.7ppm is still observed, but reduced in intensity. This signal may be indicating the presence of a higher-order polymeric species.

Sample (c).

The ^{31}P n.m.r. spectra of sample (c) at various low temperatures, to 183K, reveal a significant reduction in intensity of the septet at -62.2ppm, with a very strong broad signal at -71.1ppm with $\nu_{\frac{1}{2}}$ 200Hz.



(A)



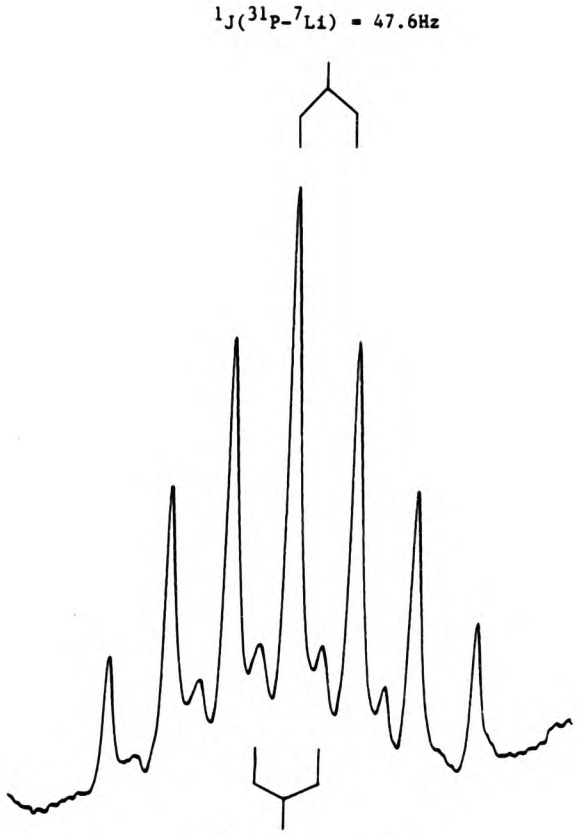
(B)

Fig. 4.13. : Schematic representation of two possible polymeric lithiated species.

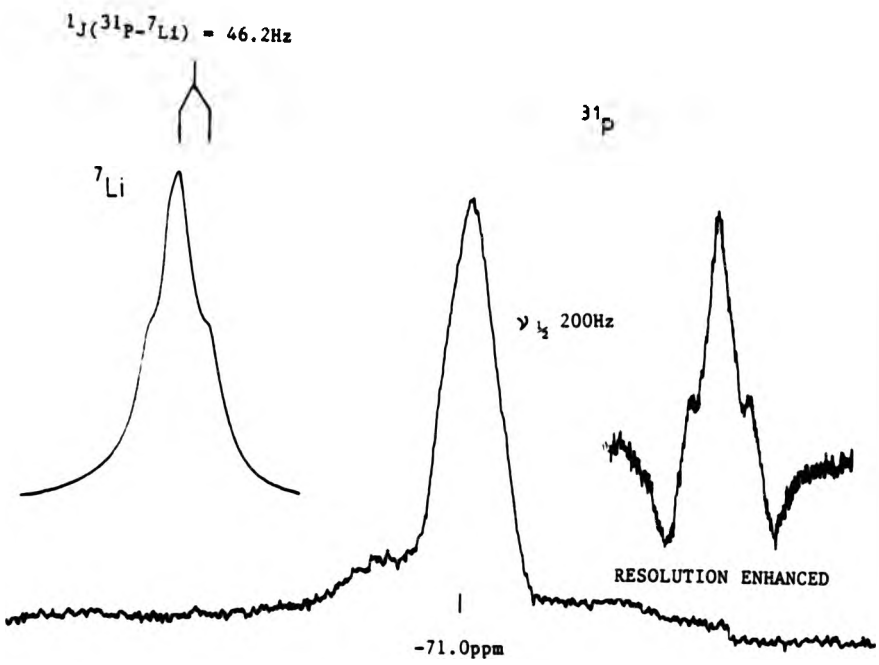
At 169K, resolution enhancement of the broad signal, seemed to reveal a degree of multiplet splitting with $^{1}J(P-{}^{7}Li)$ = 88.0Hz.(Spectrum 4.15.).

The ^{7}Li n.m.r. spectrum indicates a possible triplet with $^{1}J(P-{}^{7}Li)$ = 46.2Hz.(Spectrum 4.15.).

Spectrum 4.14. : ^{31}P n.m.r. spectrum of lithiated mppp sample (b), recorded at 193K.



Spectrum 4.15. : ^{31}P and ^{7}Li n.m.r. spectra of lithiated ▭pp sample (c), recorded at 169K.



From these results it is not possible to conclusively define a structure present in this system. The ^{7}Li n.m.r. spectrum seems to indicate a dimeric species. However, the ^{31}P n.m.r. spectra leads to the conclusion that a simple dimeric species is not present, but it may be incorporated within a larger system, as shown in Figure 4.13. From molecular model considerations, the ringed species seems feasible as it incorporates two dimeric groups within a twelve membered ring.

By comparison of the results obtained from all three samples, a stepwise lithiation process would seem to be occurring, which is observed from the initial septet to the broad signal, indicating a polymeric lithiated species.

(3). BIS-1,4-(MONOPHENYLPHOSPHINO)BUTANE, mppb.

SAMPLES (a) and (b).

The ^{31}P n.m.r spectra at 203K for both samples (a) and (b) show a symmetrical septet at δ(P) = -62.2ppm, with $^{1}J(P-^{7}Li)$ = 46.7Hz, superimposed over a broad signal; additionally, a second broad signal at δ(P) = -69.7ppm was also observed. No change in the appearance of the spectra obtained at lower temperatures was observed with sample (a). However, at 193K, the ^{31}P n.m.r. spectrum of sample (b) shows a significant decrease in the intensity of the broad signal at δ(P) = -69.7ppm, whilst the

intensity of the septet and underlying broad signal remain unchanged.

The ^{7}Li n.m.r. spectra for both samples (a) and (b) are observed as triplets, where $^{1}J(P-{}^{7}Li)$ = 46.7Hz, confirming the presence of the septet and thus a dimeric structure associated with the lithiated species of mppb. The proton-coupled ^{31}P n.m.r. spectra indicated that no P-H groups are present.

From these results it may be presumed that the septet and broad underlying signals are closely related, chemically and structurally. A possible structure to explain the presence of the resonances observed, may be a linear polymeric species, as shown in Figure 4.14.

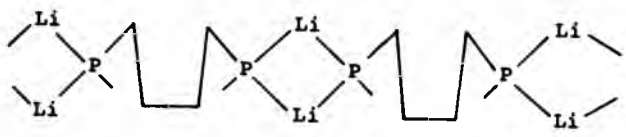


Fig. 4.14. : Schematic representation of the possible linear polymeric lithiated species observed for samples (a) and (b).

The polymeric nature of this species, could be taken to be indicated by the broad signal underlying the septet; with the interlinking dimeric groups associated with this structure, described by the septet.

A derived ring species would be composed of fourteen atoms making it highly improbable, due to the interatomic distances involved in the formation of a second dimeric form,

using two mppb molecules, and the inherent instability of a larger ring.

SAMPLE (c).

The ^{31}P and ^{7}Li n.m.r. spectra indicated the presence of similar signals as those obtained for sample (b).

SUMMARY

Table 4.7 presents all the phosphines which were lithiated and indicates the appearance of the signals observed by ^{31}P n.m.r. spectroscopy at low temperature. In all cases broad signals were observed indicating that where multiplet splittings were seen and used to identify the structure of a particular lithiated species, it cannot be taken to be the only lithiated species present, or even the major species present, but one of many other possible structures present in solution. Broad signals were found either beneath and/or very close to a multiplet structure. From the results obtained it would seem that the bulk of the substituents does not determine the structure of the lithiated species and that other factors are also responsible.

Table. 4.7.: Showing the signal observed by ^{31}P n.m.r. spectroscopy for each of the lithiated phosphines.

LITHIATED PHOSPHINE	^{31}P n.m.r. SIGNAL OBSERVED
$[PhPHLi]_3$	DECET
$[PhPDLi]_3$	DECET
"$[n\text{-}BuPHLi]_n$"	TWO BROAD SIGNALS
"$[2,4,6\text{-}Me_3C_6H_2PHLi]$"	POSSIBLY A DECET
$[Ph_2PLi]_2$	SEPTET
"$[i\text{-}Pr_2PLi]$"	DECET AND A BROAD SIGNAL
$[n\text{-}Bu_2PLi]_2$	SEPTET
$[n\text{-}Bu_2PDLi]_2$	SEPTET
"$[2\text{-}MeC_6H_4]_2PLi]_4$"	POSSIBLY A DECET
$[PhEtPLi]_2$	SEPTET AND A BROAD SIGNAL
$[Ph(n\text{-}Bu)PLi]_2$	SEPTET AND A BROAD SIGNAL
"$[2,4,6\text{-}(C(CH_3)_3)_3C_6H_2PHLi]$"	BROAD SIGNAL
"$[Ph(Li)P(CH_2)_2P(Li)Ph]$"	TWO BROAD SIGNALS
"$[Ph(Li)P(CH_2)_3P(Li)Ph]_2$"	SEPTET AND A BROAD SIGNAL
"$[Ph(Li)P(CH_2)_4P(Li)Ph]_2$"	SEPTET AND A BROAD SIGNAL
"$[Ph(Li)P(CH_2)_6P(Li)Ph]$"	SEPTET AND A BROAD SIGNAL

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CHAPTER 5.

EXPERIMENTAL

GENERAL

All reactions were carried out in an atmosphere of dry dinitrogen unless otherwise stated. Solvents were deaerated immediately prior to use and in cases where dry solvents were required, these were dried by standard methods. Many reagents used in the following syntheses were prepared by standard literature methods as indicated in the text.

CHAPTER 2.

SECTION A.

2-METHYLENE-1,3-DIPHOSPHOLANE, (X).

Butyllithium ($10.4cm^3$ of a 9.5M solution of hexane) was added in a dropwise manner to a stirred solution of 1, -bis(monophenylphosphino)ethane (12.2g, 49.4mmol) in dry Et_2O ($150cm^3$) at 0°C. When addition was complete the mixture was stirred for a further 15mins at 0°C, then was allowed to warm to room temperature and was stirred for a further 15mins.

Vinylidene chloride (4.8g, 49.4mmol) was added in a dropwise manner to the stirred mixture at 0° C. When addition was complete the mixture was stirred for a further 30mins at 0°C, then was allowed to warm to room temperature. Water ($30cm^3$) was added to the stirring mixture, the organic layer was separated and dried over $MgSO_4$. The solvent was removed under vacuum to leave an orange oily residue. Addition of MeOH afforded powdery white crystals. Recrystallised from CH_2Cl_2/MeOH as white crystals.

Yield 4g (30%)

m.p. 114-115°C.

SECTION B.

TRIPHOSPHINES.

(a) COMPOUND (VIII).

A solution containing 2,4,6-$(t\text{-}Bu)_3(C_6H_2)PH_2$(1.0g, 3.7mmol), (Xb) (1.0g, 3.7mmol) and a catalytic amount of $KOBu^t$ in dry THF ($20cm^3$) was stirred at room temperature for 15mins. The solvent was then removed under vacuum to leave an oily orange residue. Addition of EtOH yielded a waxy/oily white product which was treated with CH_2Cl_2/EtOH to give the product as white crystals.

Yield 0.3g (29%)

m.p. 52-56 °C

The analogous method using $PhPH_2$ instead of 2,4,6-$(t\text{-}Bu)_3$-$(C_6H_2)PH_2$ afforded the related triphosphine species (VII)

which was characterised in solution by ^{31}P n.m.r. spectroscopy.

(b) COMPOUND (IX).

A solution containing Ph_2PH (0.7g, 3.7mmol), (Xb) (1.0g, 3.7mmol) and a catalytic amount of $KOBu^t$ in dry THF (20cm^3) was stirred at room temperature for 15mins. The solvent was then removed under vacuum to leave an oily orange residue. Addition of EtOH (15cm^3) afforded white crystals.

Yield 0.3g (32%)
m.p. 87°C.

Analogous method using Phn-BuPH instead of Ph_2PH afforded the related triphosphine species (XI) which was characterised in solution by ^{31}P n.m.r. spectroscopy.

PENTATERTIARY PHOSPHINES.

(a) COMPOUND (XII).

A solution containing (Xb) (0.5g, 1.9mmol), $PhPH_2$ (0.1g, 0.9mmol) and a catalytic amount of $KOBu^t$ in dry THF (15cm^3) was stirred at room temperature for 15mins. The solvent was then removed under vacuum to leave an oily orange residue, which was treated with CH_2Cl_2/EtOH to yield white crystals.
Yield 0.2g (33%).
m.p. 85-86°C.

(b) COMPOUND (XIII).

A solution containing (Xb) (0.5g, 1.9mmol), (XV) (1.0g, 1.9mmol) and a catalytic amount of $KOBu^t$ in dry THF ($15cm^3$) was stirred at room temperature for 15mins. The solvent was then removed under vacuum to leave an oily orange residue. Attempts to crystallise this compound yielded the product as an oily/waxy white solid and therefore this species was characterised in solution by ^{31}P n.m.r. spectroscopy.

HEXATERTIARY PHOSPHINE

COMPOUND (XVI).

A solution containing (Xb) (0.5g, 1.9mmol), mppp (0.2g, 0.9mmol) and a catalytic amount of $KOBu^t$ in dry THF ($15cm^3$) was stirred at room temperature for 15mins. The solvent was then removed under vacuum to leave an oily orange residue. Attempts to crystallise this compound yielded the product as a white oily/waxy product, therefore this species was characterised in solution by ^{31}P n.m.r. spectroscopy.

CHAPTER 3.

SULPHURISATION OF (Xb).

A solution containing (Xb) (0.5g, 1.9mmol) and half equivalents of elemental sulphur in benzene ($10cm^3$) was stirred at room temperature for 10mins. The sample

containing the disulphurised species was isolated. The solvent was removed under vacuum to leave the product as an oily white solid. Addition of CH_2Cl_2/MeOH afforded the product as white crystals.

Yield 0.2g (33%).

m.p. 121-123° C.

Using an analogous method, compounds (IX), (XII) and (XIII) were sulphurised, to give products which were characterised in solution by ^{31}P n.m.r. spectroscopy.

CHAPTER 4.

(a) LITHIATION OF PRIMARY AND SECONDARY PHOSPHINES.

Each lithiated species was prepared by the dropwise addition of butyllithium in hexane to a freshly prepared solution of the primary or secondary phosphine in dry diethyl ether.

$RPH_2 + BuLi \rightarrow$ "[RPHLi]" + BuH

R = Ph [1-3]

= n-Bu [4]

= 2,4,6-$Me_3C_6H_2$ [5]

= 2,4,6-$(t\text{-}Bu)_3C_6H_2$ [6-11]

R_2PH + BuLi → "$[R_2PLi]$" + BuH

R = Ph [12-14]
= n-Bu [15]
= i-Pr [16,17]
= 2-MeC_6H_4 [18]
= PhEt [19,20]
= Phn-Bu [19,20]

The concentrations of the solutions prepared ranged from 0.1M to 2.5M. All the lithiations were conducted directly in a 10mm n.m.r. tube, due to the extreme air-sensitivity of the phosphines, and the air- and moisture-sensitivity of butyllithium. The samples obtained were all observed to develop a distinct orange colouration which intensified over a period of time ranging from a few hours to two days. The lithiated species were characterised in solution by ^{31}P, ^{7}Li and ^{6}Li n.m.r. spectroscopy.

(b) MIXED LITHIATED SPECIES $[Ph_2PLi_2P(n\text{-}Bu)_2]$.

Butyllithium ($0.8cm^3$ of a 2.5M solution of hexane) was added in a dropwise manner to a solution of Ph_2PH (0.4g, 2.0mmol) and $n\text{-}Bu_2PH$ (1.5g, 10.0mmol) in dry Et_2O. The lithiated species was characterised in solution by ^{31}P and ^{7}Li n.m.r. spectroscopy

(c) LITHIATION OF DISECONDARY DIPHOSPHINES.

Mppe, mppp and mppb[21-23] were lithiated in an analogous manner to (a). Three samples were prepared for each diphosphine, containing different molar ratios of BuLi to diphosphine, i.e. 1:2, 1:1 and 2:1.

INSTRUMENTATION

^{31}P n.m.r. spectra were recorded on a JEOL FX60 Fourier transform n.m.r. spectrometer operating at 24.2MHz and on a JEOL FX90Q Fourier transform n.m.r. spectrometer operating at 36.2MHz. For the spin-tickling and selective-decoupling experiments additional radio-frequencies were supplied by a Gen. Rad. model 1061 frequency synthesiser and applied *via* a tuned amplifer to an additional coil incorporated into a probe.

Samples were examined as solutions in 10mm o.d. spinning tubes at ambient temperature (21°C) unless otherwise stated. The field-frequency lock was provided by means of the ^{2}D signal from either a permanent external (D_2O) sample or in cases where higher resolution was required, from a suitable deuterated solvent added to the sample. ^{31}P spectra were recorded using appropriate spectral widths (typically 5000Hz) and sufficient data points (typically 8K) to give a digital resolution of 1.25Hz/point or better in the transformed spectrum.

Chemical shifts are expressed relative to the standard references as indicated in the text using the convention i.e. shifts to high frequency of the reference are positive.

2 Dimensional n.m.r. experiments were typically 256 data points along the t_1/f_1 axis and 1024 points along the t_2/f_2 axis. Quadrature detection was employed to prevent problems from folded signals.

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APPENDIX.

(1) ANALYSIS OF AN ABX SPIN SYSTEM.

The ABX spin system can be defined as a three-spin system with two basic groups AB and X, where A, B and X are magnetically inequivalent phosphorus nuclei. The A and B spins are strongly coupled, however, they are weakly coupled to nucleus X. Thus, the chemical shift difference between nucleus X and the other two nuclei A and B is large compared with $^{3}J(AX)$ and $^{3}J(BX)$.

The spectrum of a genuine ABX spin system displays two distinct bands. A symmetrical six-line pattern in the X basic multiplet and an eight-line pattern in the AB basic multiplet. Due to noise and overlap in an experimental ABX spectrum, the number of lines actually observed may be reduced.

The AB basic multiplet may always be decomposed into two subspectra and the total intensity of the multiplet is shared evenly by the two subspectra. One AB subspectrum involves four transitions arising in molecules which have $m_X=+1/2$ (m_X is the magnetic quantum number of $^{31}P_X$). The other AB subspectrum involves four transitions arising in molecules which have $m_X=-1/2$. The quantum mechanical analysis of the ABX spin system reveals that the four-line pattern of each one of these subspectra display a mirror-image symmetry. Each satisfies the same relationship between transition frequencies and relative intensities as that of an AB spin system, i.e. intensity ratios of the inner and outer lines. A and B are separated by a chemical shift

which is nearly of the order of magnitude as the coupling constant $^{2}J(^{31}P_{A} - ^{31}P_{B})$. (Fig. A.1.)

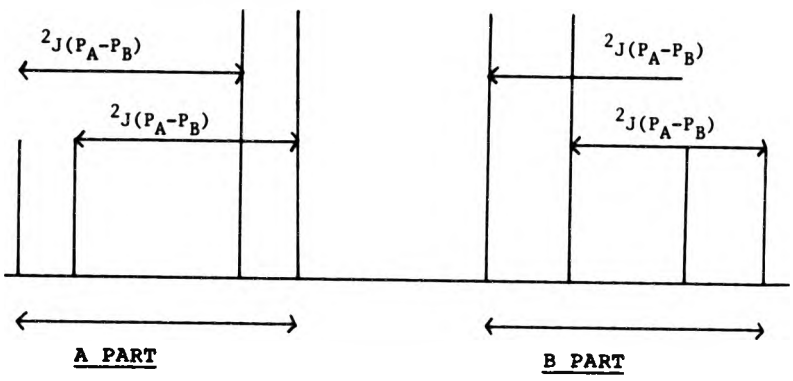

Fig. A.1. : Schematic representation of the AB part of an ABX spin system.

Theoretically the X part of the spectrum consists of a six-line pattern (Fig. A.2).

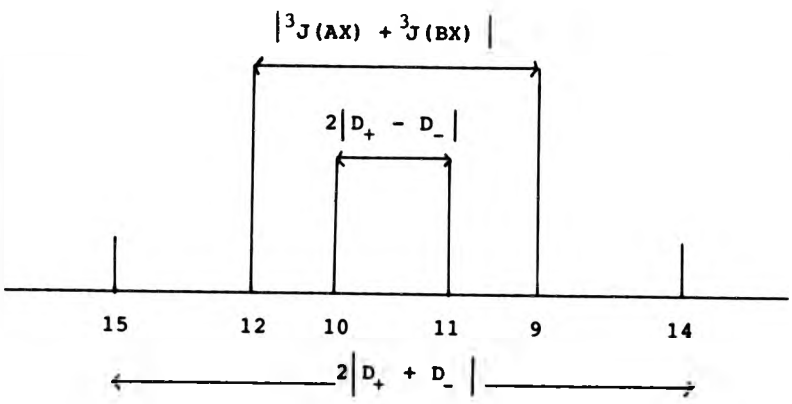

Fig. A.2. : Theoretical representation of the X part of an ABX spin system.

The two transitions 14 and 15 shown in Figure A.2. need not always be situated outside the X lines. The relative intensities of the X frequencies are found to depend upon the magnitude of $(\nu_A - \nu_B)$ and upon the relative signs of $^3J(AX)$ and $^3J(BX)$. Transitions 14 and 15 are found to have an appreciable intensity when $(\nu_A - \nu_B)$ becomes small and when $^3J(AX)$ is of opposite sign to $^3J(BX)$.

The X basic multiplet is also found to collapse into a 1:2:1 triplet when $^3J(AX)$ $^3J(BX)$, with the signs of the two coupling constants being the same.

(2) ANALYSIS OF AN AA'X SPIN SYSTEM.

An AA'X spin system is generally described as a 'deceptively simple ABX spin system'. In this study AA'X spin systems have been encountered in the analysis of the ^{13}C n.m.r. spectra of phenyl carbon atoms, for example ligand X. In these systems A, A' = phosphorus atoms and X = phenyl carbon atoms.

AA'X spin systems may be described by the parameters N, L and J where,

$$N = J(AX)+J(A'X)$$

$$L = J(AX)-J(A'X)$$

$$J = J(AA')$$

The X part (i.e. ^{13}C) of the AA'X spectrum consists of six lines, of which two (the N lines) are strong and of equal intensity, separated by N and have a combined intensity equal to half of the X spectrum.

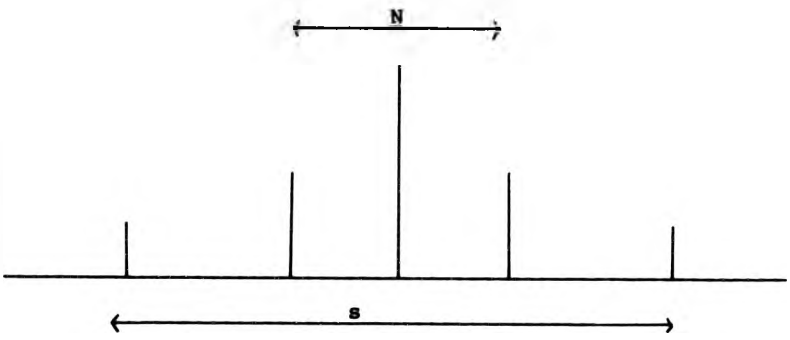

Fig. A.3. : A schematic representation of the X part of an AA'X spin system.

Centrally positioned between the N lines are two degenerate transitions. The remaining two lines of equal intensity and symmetrically placed about the central degenerate pair of lines, they may occur within or outside of the N lines, their separation is given by s. (see Fig. A.3).

$$s = 2\sqrt{(J(AX) - J(A'X))^2 + J(AA')^2}$$

If J(AA') is very large, then only three lines will be observed, i.e. the two N lines and the central degenerate pair of lines, with the outer s lines very weak and far apart, which can be difficult to observe as they can be lost in the baseline noise. Thus, as the value of J(AA') becomes smaller, the outer two s lines begin to appear closer to the N lines, hence five lines of an AA'X spectrum are observed.

PHOSPHORUS RESONANCE INTENSITY DISTORTION.

It is likely that the different types of phosphorus in the AMX system will have different relaxation times (T values) and hence in order to obtain accurate relative intensities, it would be necessary to pulse very slowly during acquisition of the spectra. In practice this was not convenient, and therefore there is some distortion of the apparent relative intensities.

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